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AN ALL-AMERICAN SANITARY-WARE BODY*

By I. E. Sproat, C. C. Treischel, and E. W. Emrich

Abstract

The development of a casting body for sanitary ware is based on the theories that (1) organic deflocculating agents are inherently better than inorganic deflocculants; (2) the use of at least three ball clays and two kaolins permits better control of uniformity of physical properties of casting slip; and (3) the proper selection of domestic clays will give casting slips that cast as fast or faster than those made from imported clays. Comparisons with commercial bodies are made for color, shrinkage, absorption, speed of casting, and rate of thickening.

I. Introduction

This study of domestic clays for use in sanitary-ware casting bodies was started in July, 1939, in order to increase the use of domestic clays for casting bodies. Although such bodies have been easier to develop from English clays, the present conditions in Europe make the development of domestic clays for casting an important contribution in this country.

Studies in this laboratory, as well as the statements of ceramic engineers in many plants, furthermore, indicate that casting slips made from imported clays have a fairly short casting range (see Fig. 1, curve No. 4). The use of organic dispersing agents has been reported[1] to be helpful in increasing the casting range, but the present study will show that the proper selection of raw materials will also have a beneficial effect in this respect. The term "casting range" means the allowable variation in the amount of dispersing agent that may be added without affecting the workability of the slip.

The casting efficiency has also been tested for a certain domestic kaolin that has been produced continuously from the same mine since Civil War days. The uniform behavior of this kaolin has been established through use over a long period of years in the production of chemical porcelain, electrical porcelain, floor and wall tile, and, to a limited extent, sanitary ware. The rate of settling and the reaction to sodium silicate as compared with a good English china clay (see Tables I and II) shows promising results from the preliminary tests.

II. Procedure

Because of a theory of the writers that the use of several clays in any whiteware body tends to insure uniformity and small variations in raw materials have a greater effect on casting slips than on plastic or dry-pressed bodies, the tests were conducted with at least three kaolins and three ball clays in each body. Based on casting rate, a combination of kaolins used in body No. 5 was selected as shown in Table III. Commercial casting slips obtained from four sanitary-ware plants (bodies Nos. 1, 2, 3, 4d, 4s) as well as body "ISJ" from Earhart's study[2] of nepheline syenite and North Carolina kaolin (body No. 6) were used for a comparative analysis.

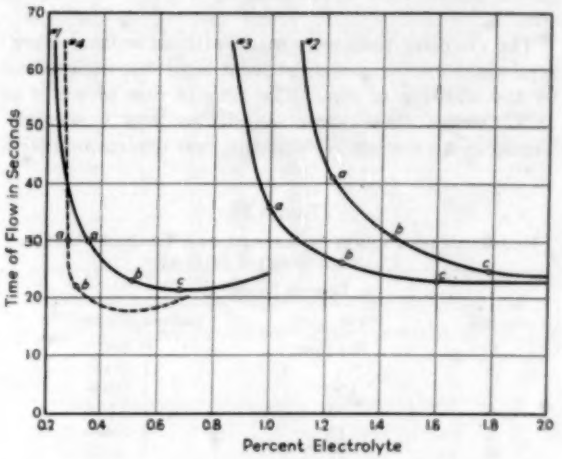

Fig. 1.—Viscosity curves for sanitary-ware body No. 5.

(1) Method of Preparing Slips

The slips were made up from a 9000-gm. batch. The clays were first dispersed in sufficient water to produce a specific gravity of about 1.8, to which had been added just enough electrolyte to produce a fluid slip. The nonplastics and the minimum amount of electrolyte to produce a slip that could be screened through a 100-mesh screen were added. The water content of the

Table I

Settling Rate of Peerless Kaolin and English China Clay No. 333

Settling time (min.)	Clear liquid on top (cc.)	
	Peerless kaolin	English china clay No. 333
5	28	6
10	76	12
15	124	46
20	142	86
30	152	132
60	164	148

* A preliminary report on this subject was presented at the Forty-Second Annual Meeting, The American Ceramic Society, Toronto, Canada, April 7–13, 1940 (White Wares Division); revised and extended copy received June 26, 1941.

[1] I. E. Sproat, C. C. Treischel, and E. W. Emrich, "Use of Organic Dispersing Agents in Casting Slips," *Bull. Amer. Ceram. Soc.*, **19** [2] 47–48 (1940).

[2] W. H. Earhart, "Use of North Carolina Kaolin in Casting Bodies," *ibid.*, **19** [5] 163–68 (1940).

screened slip was determined, and the large batch was divided into eight small portions, each containing 800 gm. of solids. Varying amounts of electrolyte were added to these small batches, which were placed in Mason jars. The jars were shaken vigorously and allowed to stand overnight. The following morning they were placed in a shaking machine for five hours and tested.

This method of preparation was found to yield consistent results. Tap water with a pH of 7.8 to 8.1 was used throughout this investigation in order to obtain results more closely related to those in factory practice than with the use of distilled water.

(2) Tests

The shrinkage, absorption, and modulus of rupture data were obtained in the usual manner from cast test pieces, which were approximately 1 by 1 by 8 in. in size.

The viscosity tests were made with an ordinary flow-type viscosimeter, and a constant head was maintained by the addition of slip. The time of flow of water at 28°C. under these same conditions was 6 seconds. Tendency to thicken on standing was determined with a Stormer viscosimeter,[3] and the casting rate was measured by pouring the slip into a 4-in. disk mold and allowing it to cast for 30 minutes. The excess slip was

TABLE II

REACTION OF PEERLESS KAOLIN AND ENGLISH CHINA CLAY TO SODIUM SILICATE

Slip No.	Flow (sec.)	Sodium silicate (%)
	Peerless kaolin*	
1	No flow	0.9875
2	" "	1.0000
3	120	1.0500
4	35	1.1125
5	18	1.3000
6	17.5	1.4875
7	17	1.7375
	English china clay No. 333†	
1	No flow	0.9688
2	163	1.0403
3	120	1.1833
4	106	1.5410
5	137	1.6835
6	137	1.8263
7	158	2.0400

* Slip temp., 27°C.; water, 30.7%; sp. gr., 1.747.
† Slip temp., 28°C.; water, 35.4%; sp. gr., 1.668.

TABLE III

CASTING RATE OF PEERLESS KAOLIN COMBINED WITH OTHER DOMESTIC KAOLINS

Batch No.	Kaolin composition 50%	Test piece cast 30 min., wet weight (gm.)
1	Peerless No-Karb	113.83
2	Peerless Lunday N.C.	96.03
	33⅓%	
3	Peerless No-Karb Lunday N.C.	141.37

Clay in slip, 67.75%; water in slip, 32.25%; sodium silicate for dispersion, 1.2%.

TABLE IV

ABSORPTION AND SHRINKAGE OF BODY COMPOSITIONS

	Body No. 5	6	7	8	9
	Composition (%)				
Jasper flint	18.0	22.0	18.0	18.0	5.0
A-2 N.C. feldspar	32.0		33.0	33.0	31.0
Nepheline syenite		28.0			
Ball clay					
Jernigan	6.0	10.0		6.0	
Old Mine No. 4		7.5	9.0	6.0	9.0
Ky. No. 12		7.5			
Wade No. 5			10.0	8.0	10.0
KCM	6.0		6.0	6.0	6.0
Tenn. No. 5	8.0				
Kaolin					
Lunday	10.0		8.0	6.0	8.0
Kamec		25.0			
Peerless	10.0		10.0	9.0	10.0
Ga. No. 27			6.0	8.0	6.0
No-Karb	10.0				
HS Pyrax pyrophyllite					15.0
Cone No.	Absorption of dry weight (%)				
6	8.3	3.7	3.8	3.8	4.3
7	4.9	2.2	2.4	2.3	3.6
8	2.8	0.9	0.8	0.6	1.8
9	1.5	0.4	0.3	0.1	0.3
10	0.1	0.0	0.0	0.0	0.0
11	0.0	0.0	0.0	0.0	0.0
12	0.0	0.0	0.0	0.0	0.0
	Total shrinkage of cast length (%)				
6	8.2	12.0	12.1	12.2	10.4
7	11.3	12.6	12.5	12.7	11.4
8	11.7	12.9	12.7	13.1	12.5
9	12.1	13.5	13.1	13.4	13.0
10	13.2	13.5	13.5	13.7	13.1
11	13.3	13.6	13.6	13.8	13.1
12	13.3	13.0	13.6	13.8	13.2

TABLE V

ABSORPTION AND SHRINKAGE OF COMMERCIAL BODIES

Cone No.	Body No. 1	2	3	4d	4s
	Absorption of dry weight (%)				
6	7.0	4.0	4.7	3.5	3.5
7	2.5	1.3	1.5	2.1	2.1
8	1.5	0.7	0.9	1.4	1.4
9	0.2	0.2	0.4	0.2	0.2
10	0.0	0.0	0.0	0.0	0.0
11	0.0	0.0	0.0	0.0	0.0
12	O.F.	O.F.	0.0	0.0	0.0
	Total shrinkage of cast length (%)				
6	9.7	10.1	11.5	10.6	10.5
7	11.5	11.4	12.5	11.4	11.0
8	11.8	11.8	12.6	12.3	12.5
9	12.2	12.0	12.9	12.9	12.7
10	12.9	12.1	13.7	12.9	12.9
11	13.0	11.8	13.7	13.0	13.0
12	10.9	10.7	13.6	13.0	13.0

O.F. = overfired.

[3] See p. 48 of footnote 1.

drained, and the test piece was "scrapped" and weighed as soon as it released from the mold. This wet weight was recorded as the casting rate. (Although the efficacy of this test has been questioned for use in studies on sanitary ware and electrical porcelain bodies, it will be used by most investigators until something better is generally accepted.)

A periodic gas-fired test kiln was used to fire the test pieces; the firing period was 22 hr.; and the specimens were cooled for 18 hr.

Comparisons of the fired color were made on 4-in. disks with a Higgins colorimeter.

III. Results

(1) Absorption and Shrinkage

The vitrification behavior of bodies Nos. 6, 7, 8, 9 and of the four commercial bodies is essentially the same; body No. 6 shows slight overfiring at cone 12, and body No. 5 (low in ball clay) seems to be underfired.

(2) Modulus of Rupture

Bodies Nos. 6, 7, and 9 have good dry strength and compare favorably with the commercial bodies; body No. 8 perhaps is a bit weak for use under some factory conditions, and body No. 5 shows the lack of sufficient bonding clays.

An interesting feature of the green transverse strength tests is the increase noted when clay deflocculant is used as a dispersing agent. This increase ranges from 10.0% in body No. 5 to 19.0% in body No. 9.

The fired strength, on the other hand, does not seem to be affected by this type of dispersing agent. The differences that occur are either within possible error in making the test or they may be explained by the nature of the fracture of the fired test piece which is given in the fracture data (p. 315).

TABLE VI

PROPERTIES OF SLIPS USED FOR STRENGTH TESTS*

Slip No.	Electrolyte (%)		Flow (sec.)	Water (%)	Specific gravity
5-a	Soda ash	0.178			
	Sodium silicate	0.333	23	26.8	1.838
5-b	Clay deflocculant No. 5	1.25	26	26.6	1.827
6-a	Soda ash	0.185			
	Sodium silicate	0.531	59	26.9	1.818
6-b	Clay deflocculant No. 2	1.000			
	Sodium silicate	0.550	66	27.4	1.808
7-a	Soda ash	0.050			
	Sodium silicate	0.0625	41	26.5	1.832
7-b	Clay deflocculant No. 2	0.85	44	26.1	1.837
8-a	Soda ash	0.100			
	Sodium silicate	0.125	57	26.7	1.828
8-b	Sodium silicate	0.235			
	Clay deflocculant No. 2	1.000	58	27.0	1.820
9-a	Soda ash	0.050			
	Sodium silicate	0.135	67	26.5	1.838
9-b	Clay deflocculant No. 2	1.50	69	27.1	1.820
Drain, commercial body No. 4			39	26.3	1.840
Solid, commercial body No. 4			85	25.6	1.857

* The difference in viscosity results between Table VI and those given for the same bodies in Tables IX to XII is due to the fact that the slips used for the strength tests were not blunged or shaken for several hours after standing overnight but were just stirred for a few minutes by hand.

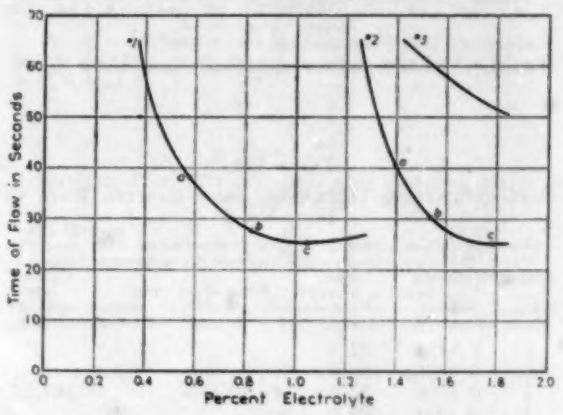

FIG. 2.—Viscosity curves for sanitary-ware body No. 6.

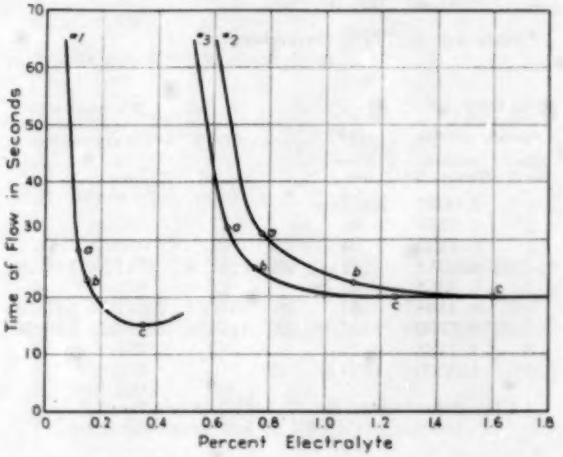

FIG. 3.—Viscosity curves for sanitary-ware body No. 7.

TABLE VII

MODULUS OF RUPTURE DATA

Slip No.	Body No. 5		6		7		8		9		Commercial body No. 4	
	a	b	a	b	a	b	a	b	a	b	Drain(d)	Solid(s)
	Modulus of rupture (lb./sq. in.) at cones 10–11											
Green strength	300	330	500	550	426	480	328	378	487	580	600	540
Fired strength			7900	7300	9050	8150	7720	8180	8070	7890	7720	7700

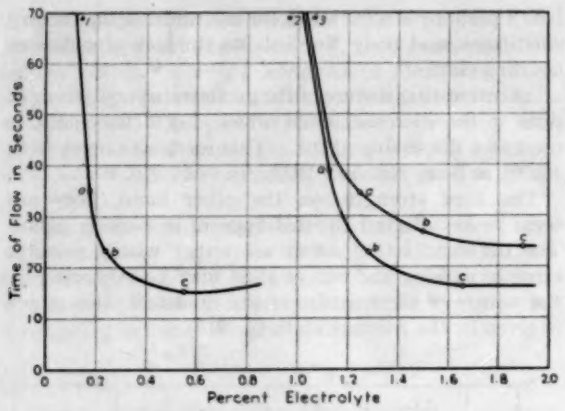

FIG. 4.—Viscosity curves for sanitary-ware body No. 8.

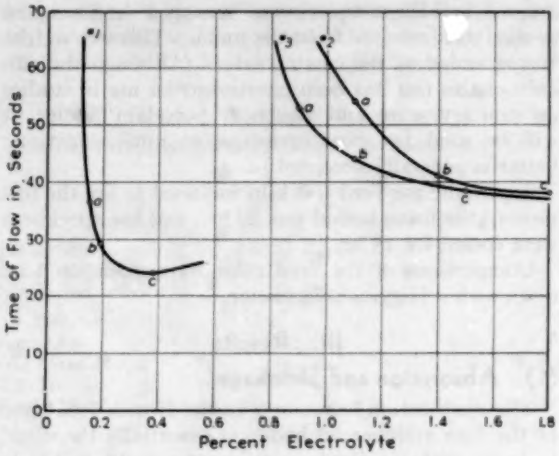

FIG. 5.—Viscosity curves for sanitary-ware body No. 9.

TABLE VIII

DEFLOCCULATION, THICKENING, AND CASTING RATE OF BODY NO. 5

Slip temp. (°C.)		28						
Water (%)		26.4						
Specific gravity		1.838						
			No. of revolutions on Stormer viscosimeter					
			Time of set (min.)					
Slip No.*	Sodium silicate (%)	Flow (sec.)	0	2	5	10	15	Casting rate (gm./30 min.)
1	0.1111	37.5						
2	0.1388	33.0						
3	0.1666	30.0	14	10	8	5	4	163.25
4	0.1934	28.0						
5	0.2222	27.0						
6	0.3340	23.0	34	34	34	34	30	143.41
7	0.5000	21.5	44	44	44	44	44	128.38
8	0.5453	23.0						

* Soda ash, 0.1777% throughout.

Slip temp. (°C.)		29						
Water (%)		26.5						
Specific gravity		1.830						
Slip No.†	Sodium silicate (%)	Flow (sec.)						
1	0.0022	No flow						
2	0.0577	86						
3	0.1133	64						
4	0.2244	41	16	12	8	6	5	181.29
5	0.3355	35						
6	0.4466	31	26	26	24	22	22	167.58
7	0.7799	25	32	34	34	32	32	148.50
8	1.1133	24						
9	1.2500	24						

† Clay deflocculant No. 2, 1.00% throughout.

Slip temp. (°C.)		29						
Water (%)		26.4						
Specific gravity		1.827						
Slip No.	Clay deflocculant No. 5 (%)	Flow (sec.)						
1	0.8220	75						
2	0.9333	45						
3	1.0440	36	16	12	8	5	5	175.33
4	1.1550	29						
5	1.2666	26	24	24	24	18	18	165.81
6	1 3777	25						
7	1.5990	23	36	32	32	32	40	157.72
8	1.8222	23						

TABLE IX

DEFLOCCULATION, THICKENING, AND CASTING RATE OF BODY NO. 6

Slip temp. (°C.)		28						
Water (%)		26.7						
Specific gravity		1.820						
			No. of revolutions on Stormer viscosimeter					
			Time of set (min.)					
Slip No. 6-1*	Sodium silicate (%)	Flow (sec.)	0	2	5	10	15	Casting rate (gm./30 min.)
1	0.155	88						
2	0.187	71						
3	0.217	60						
4	0.280	48						
5	0.343	43						
6	0.405	38	14	10	6	3	2	113.16
7	0.655	28	26	26	24	24	20	99.59
8	0.875	25	32	32	32	30	30	95.44
9	1.073	26						

* Soda ash, 0.177 throughout.

Slip temp. (°C.)		27						
Water (%)		26.8						
Specific gravity		1.819						
Slip No. 6-2†	Sodium silicate (%)	Flow (sec.)						
1	0.1660							
2	0.2990	75						
3	0.2910	56						
4	0.3540	46						
5	0.4165	40	12	6	2	1		116.57
6	0.4890	33						
7	0.5415	30	21	15	12	10	8	109.38
8	0.7915	25	24	24	22	21	20	100.21

† Clay deflocculant No. 2, 1.000% throughout.

Slip temp. (°C.)		27.5						
Water (%)		26.8						
Specific gravity		1.820						
Slip No. 6-3	Clay deflocculant No. 5 (%)	Flow (sec.)						
1	1.0555	91						
2	1.3055	70						
3	1.5555	60						
4	1.8055	51.5						
5	2.0555	47						
6	2.3000	44.5	Too thick to test					115.01
7	2.5555	44.5	"	"	"	"		111.32

Body No.	Fracture data on fired ware (10 test pieces for each body)
6-a	All had crack in center; several were almost 1/2 in. long.
6-b	Same as No. 6-a.
7-a	One bar had a very small crack; others had small 1/8-in. "ball" in center; fracture better than commercial body but not quite so good as No. 9-a.
7-b	Same as No. 7-a.
8-a	About as good as No. 7-a.
8-b	" " " " " "
9-a	One bar had a small "ball" in center; nine bars broke with a clean smooth fracture; best of the series.
9-b	About like No. 7-a.

Commercial body No. 4: three bars had very small cracks; others, small "balls."

The slight tendency to balling shown by most of the bodies could doubtless be completely overcome by a better adjustment of the electrolyte. The fired strengths were well within the limits of good commercial bodies.

TABLE X

DEFLOCCULATION, THICKENING, AND CASTING RATE OF BODY NO. 7

Slip temp. (°C.)	27
Water (%)	26.2
Specific gravity	1.830

Slip No. 7-1*	Sodium silicate (%)	Flow (sec.)	No. of revolutions on Stormer viscosimeter, Time of set (min.) 0	2	5	10	15	Casting rate (gm./30 min.)
1	0.0500	37						
2	0.0562	32						
3	0.0625	28	20	10	6	4	3	113.60
4	0.0750	26						
5	0.0875	24	30	22	20	17	14	91.35
6	0.1000	23						
7	0.1375	19						
8	0.2000	16	86	86	86	86	84	78.10
9	0.3000	15						
10	0.4000	16						

* Soda ash, 0.0500% throughout.

Slip temp. (°C.)	28
Water (%)	26.4
Specific gravity	1.830

Slip No. 7-2	Clay deflocculant No. 2 (%)	Flow (sec.)						
1	0.630	60						
2	0.670	49						
3	0.775	31	20	12	8	4	2	116.32
4	0.850	28						
5	1.100	22.5	26	23	22	20	19	95.92
6	1.350	20.5						
7	1.600	20.0	24	24	22	22	22	87.94
8	2.100	20.0						

Slip temp. (°C.)	27.5
Water (%)	26.4
Specific gravity	1.828

Slip No. 7-3	Clay deflocculant No. 5 (%)	Flow (sec.)						
1	0.500	98						
2	0.550	58						
3	0.600	42						
4	0.650	32	16	9	6	2	1	120.13
5	0.700	27						
6	0.750	25	34	30	24	22	18	106.50
7	1.000	21						
8	1.250	20	48	48	48	48	48	85.58

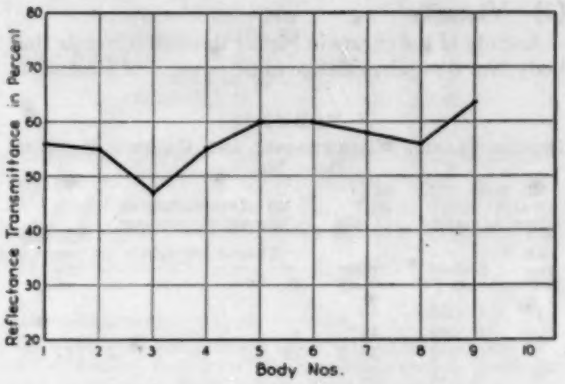

FIG. 6.—Whiteness comparisons (455 mμ) on commercial bodies Nos. 1, 2, 3, and 4 and on test bodies Nos. 5, 6, 7, 8, and 9.

TABLE XI

DEFLOCCULATION, THICKENING, AND CASTING RATE OF BODY NO. 8

Slip temp. (°C.)	27
Water (%)	26.6
Specific gravity	1.825

Slip No. 8-1*	Sodium silicate (%)	Flow (sec.)	No. of revolutions on Stormer viscosimeter, Time of set (min.) 0	2	5	10	15	Casting rate (gm./30 min.)
1	0.050	52						
2	0.075	35	27	19	15	12	10	128.13
3	0.106	26						
4	0.125	24						
5	0.137	23	42	39	35	32	30	103.08
6	0.200	20						
7	0.263	18						
8	0.450	15.5	63	63	60	58	58	76.45
9	0.700	16						

* Soda ash, 0.100% throughout.

Slip temp. (°C.)	28
Water (%)	26.9
Specific gravity	1.826

Slip No. 8-2†	Sodium silicate (%)	Flow (sec.)						
1	0.065	57						
2	0.096	48						
3	0.127	39	22	14	10	5	3	123.44
4	0.158	32						
5	0.221	26						
6	0.283	23	40	38	34	32	30	100.27
7	0.408	19						
8	0.658	16	56	56	56	52	52	87.63
9	0.800	16						

† Clay deflocculant No. 2, 1.00% throughout.

Slip temp. (°C.)	27
Water (%)	26.5
Specific gravity	1.826

Slip No. 8-3	Clay deflocculant No. 5 (%)	Flow (sec.)						
1	1.050	65						
2	1.125	44						
3	1.250	34.5	28	20	16	12	12	128.31
4	1.375	30						
5	1.500	27	30	27	26	22	20	113.63
6	1.750	24						
7	2.000	24	28	26	25	21	20	106.33
8	2.500	24						

(3) Viscosity

A study of the curves in Figs. 1 through 5 reveals that body No. 6 requires the greatest amount of electrolyte to produce maximum dispersion, whereas body No. 7 takes the least; bodies Nos. 6 and 9 are not readily dispersed with clay deflocculant.

From the standpoint of electrolyte requirements and maximum fluidity, body No. 7 is the best and body No. 8 a close second. It is to be noted further that clay deflocculant gives a much longer casting range than soda ash and sodium silicate.

TABLE XII

DEFLOCCULATION, THICKENING, AND CASTING RATE OF BODY NO. 9

Slip temp. (°C.) 28
Water (%) 26.7
Specific gravity 1.828

Slip No. 9-1*	Sodium silicate (%)	Flow (sec.)	No. of revolutions on Stormer viscosimeter, Time of set (min.) 0	2	5	10	15	Casting rate (gm./30 min.)
1	0.083	48						
2	0.089	41						
3	0.102	36.5	12	7	5	3	2	117.52
4	0.121	32						
5	0.146	29	16	13	12	10	9	104.51
6	0.208	25						
7	0.333	24	28	28	28	26	26	87.41
8	0.450	25						

* Soda ash, 0.05% throughout.

Slip temp. (°C.) 27
Water (%) 26.6
Specific gravity 1.822

Slip No. 9-2	Clay deflocculant No. 2 (%)	Flow (sec.)						
1	0.90	78						
2	1.00	62						
3	1.10	54	10	7	5	3	2	119.40
4	1.20	48						
5	1.40	41	10	9	8	7	6	110.43
6	1.60	38.5						
7	1.80	38	12	11	11	10	10	104.27
8	2.00	38						

(4) Thickening on Standing (Thixotropy)

All casting slips have some tendency to thicken if they are allowed to remain immobile. The tests indicate that the Stormer viscosimeter is a good instrument to use for measuring this trend. The data in Tables VIII through XII show that as minimum viscosity is approached the tendency to thicken decreases. These

TABLE XII (*concluded*)

Slip temp. (°C.) 28
Water (%) 26.7
Specific gravity 1.828

Slip No. 9-3	Clay deflocculant No. 5 (%)	Flow (sec.)	No. of revolutions on Stormer viscometer, Time of set (min.) 0	2	5	10	15	Casting rate (gm./30 min.)
1	0.80	68						
2	0.90	53	9	6	5	3	2	119.63
3	1.00	47						
4	1.10	44	11	11	9	8	8	111.20
5	1.30	40.5						
6	1.50	38.5	11	11	10	9	8	106.61
7	1.70	37.5						
8	2.00	37.0						

TABLE XIII

VISCOSITY, SPECIFIC GRAVITY, THICKENING, AND CASTING RATE OF COMMERCIAL BODIES

Slip No.*	Flow (sec.)	Specific gravity	Water (%)	No. of revolutions on Stormer viscosimeter, Time of set (min.) 0	2	5	10	15	Casting rate wet weight (gm./30 min.)
1	32	1.830	26.5	6	5	4	2	2	119.67
2	23	1.850	25.4	22	16	14	10	8	116.88
3	23	1.810	27.8	16	12	8	5	4	103.35
4 drain	39	1.840	26.3	12	11	9	7	6	106.70
4 solid	85	1.857	25.6	4	1				120.91

* Temperature, 28°C. throughout.

TABLE XIV

COLOR COMPARISONS (HIGGINS COLORIMETER)

Body No.	Reflectance transmittance (%), Wave length (mμ)† 430	455	460	490	530	570	610	650	700
1*	55.0	56.0	56.0	59.7	62.0	63.0	63.5	64.0	65.8
2*	54.0	55.0	55.2	59.3	61.2	63.5	64.2	65.0	66.3
3*	46.0	46.8	47.0	50.0	52.8	54.4	55.7	56.5	58.5
4*	54.1	55.2	55.8	59.0	62.0	64.0	65.2	66.8	68.4
5	58.5	59.7	60.0	63.0	65.2	67.1	68.0	69.0	70.0
6	59.0	60.2	60.9	63.8	66.8	67.9	68.7	69.9	70.7
7	57.1	58.1	58.8	62.4	65.2	67.1	68.7	70.0	70.8
8	56.0	56.0	57.7	61.0	64.1	66.4	68.0	69.3	70.1
9	62.2	63.7	64.2	67.1	69.1	70.0	71.0	72.3	72.9

* Visible white, 455 mμ.
† Commercial bodies.

results seem to agree with plant experience on slips for solid (core) casting and drain casting, that is, the best point on the deflocculation curve of a given body for solid casting is never the same as the best point for drain casting and vice versa. Viscosity and Stormer tests on bodies Nos. 4s and 4d show the practical aspects of this conclusion.

No marked difference is noted in the tendency of the five test bodies to thicken on standing; bodies Nos. 7 and 8, however, which have greater fluidity than the others would doubtless give less trouble in the casting shop.

(5) Casting Rate

Body No. 5 casts faster than the others, probably owing to the low ball clay content; body No. 8 is next in casting rate, and there is only a slight difference between bodies Nos. 6, 7, and 9. A comparison with the commercial bodies shows that the test bodies stand up well.

The clay deflocculant produces the fastest casting slips in all tests, and the rate is not decreased as much with increasing additions of electrolyte as when sodium silicate and soda ash are used as dispersing agents.

(6) Fired Color

The ratings on fired color are as follows:

Commercial body No. 3	Worst
Commercial bodies Nos. 1, 2, 4	
Test body No. 8	
Test bodies Nos. 5, 6, 7	
Test body No. 9	Best

Inasmuch as the ordinary eye can easily distinguish a difference of 0.5 in the 455-mμ figures (shown in Table XIV and for comparison in Fig. 6), the color of test bodies as a group is considerably better than that of the commercial bodies.

Acknowledgment

The raw materials used in this study came from the following sources, and grateful acknowledgment is made to these companies: Jasper flint, Pennsylvania Pulverizing Co.; A-2 N.C. feldspar, Consolidated Feldspar Co.; nepheline syenite, Great Lakes Foundry Sand Co.; Jernigan ball clay, H. C. Spinks Clay Co.; Old Mine No. 4 ball clay, Ky. No. 12 ball clay, Wade No. 5 ball clay, and Tenn. No. 5 ball clay, Kentucky-Tennessee Clay Co.; KCM ball clay, Kentucky Clay Mining Co.; Lunday kaolin, Harris Clay Co.; Kamec kaolin, Kaolin, Inc.; No-Karb kaolin, Edgar Bros. Co.; Ga. No. 27 kaolin, Moore and Munger; Peerless kaolin and HS Pyrax pyrophyllite, R. T. Vanderbilt Co.

The R. T. Vanderbilt Company
230 Park Avenue
New York, N. Y.

FURTHER INVESTIGATIONS IN THE IMPROVEMENT OF CLAYS THROUGH CONTROL OF pH AND CHARACTER OF BASE-EXCHANGE SATURATION*

By George J. Barker and Emil Truog

Abstract

Marked improvement in the workability of clays and the quality of the fired products can be attained with many clays by a control process that involves the regulation of pH and the character of base saturation by the addition of sodium carbonate and other alkaline materials. The amount of basic material which must be added to effect this proper control is most easily determined by the use of titration curves derived by titrating samples of the clays with alkali. The interpretation of the various types of curves thus obtained is discussed in detail. The control process, if desired, may be used in combination with deairing. The use of certain wetting agents in addition to the control process has given only slight additional benefit.

I. Introduction

The authors in previous publications[1] have disclosed that if the pH, character of base saturation (considerable saturation with sodium), and soluble salt content of a clay are properly adjusted and controlled before forming into ware for structural clay products, marked improvements result in the workability of the clay and in the physical properties of the ware made from the clay. Ten improvements were enumerated in this connection, and subsequent operations in commercial plants[2] have demonstrated the soundness of the conclusions drawn from extensive laboratory tests.

It has also been disclosed[1(b)] that the most favorable pH adjustment for a particular clay falls at or near the break in the slope of the titration curve in the alkaline region, which is obtained on plotting the percentages of sodium carbonate added to this clay (as abscissas) against the resulting pH values of the clay (as ordinates). The curves obtained with various clays have been classi-

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 2, 1941 (Structural Clay Products Division). Received April 2, 1941.

[1] (*a*) G. J. Barker and Emil Truog, "Improvement of Stiff-Mud Clays Through pH Control," *Jour. Amer. Ceram. Soc.*, **21** [9] 324–29 (1938); (*b*) G. J. Barker and Emil Truog, "Factors Involved in Improvement of Clays Through pH Control," *ibid.*, **22** [9] 308–12 (1939).

[2] Anon., "Putting 'New Life' into Surface Clay by Adding Soda Ash," *Brick Clay Record*, **93** [2] 12–13 (1938).

fied into three general types,[10] which are reproduced in Fig. 1. Additional information subsequently obtained regarding the character and behavior of clays that give these three types of curves is presented in this paper.

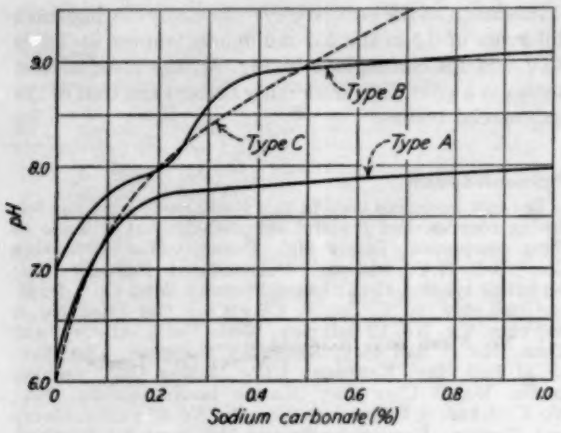

FIG. 1.

II. Titration Methods and Curves

For the benefit of those unfamiliar with the methods used, a brief description of the titration procedures commonly followed and the plotting and interpretation of the results thus obtained are presented.

To titrate a clay, weigh out a series of eleven representative 20-gm. samples (dry basis) of the clay in the same moist condition as it is used in the factory. Transfer each sample to a beaker and add distilled water and varying amounts of sodium carbonate solution so that the final dilution in each case will consist of 50 cc. of liquid. Sample No. 1 is usually treated with water alone; sample No. 2, with water plus 0.1% of sodium carbonate (calculated on the dry-weight basis of clay); and succeeding samples, with increasing amounts of sodium carbonate in steps of 0.1% so that sample No. 11 receives 1%. After making these additions, stir the samples vigorously several times during 30 minutes after which the pH of the clay suspension may be determined by means of a pH meter equipped with a glass electrode.

An alternate titration procedure is given, which in some respects is simpler and gives more uniformly consistent curves. Place a 10-gm. sample of the clay (20-mesh air-dried) in a 250-cc. beaker, add 100 cc. of distilled water, and allow to soak for at least 1 hr. Titrate with a 0.5% solution of sodium carbonate by means of a titration assembly equipped with a mechanical stirring device, a pH meter, and a shielded glass electrode. Add the sodium carbonate solution in increments of 1 cc. so that each increment is equivalent to an addition of 0.05% of sodium carbonate. After each addition, allow the suspension to be stirred until the pH reading becomes practically constant, which usually occurs after three or four minutes of stirring. The vigorous stirring, which is interrupted during a pH reading, gives greater assurance of the attainment of equilibrium than in the first procedure and thus often gives smoother curves.

The form of the curve derived on plotting the titration results and the region where the break in the slope of the curve takes place are influenced to some extent by the titration procedure used. These two procedures, however, give substantially the same results for the desirable treatment of a clay.

The titration curve is obtained by plotting as abscissas the percentages of sodium carbonate added against the pH values obtained as ordinates, and it consists, in the alkaline region, of two portions. These parts of the curve may be distinguished from each other by the relative magnitudes of their slopes which are governed by the amount of increase in the pH of the clay by the addition of known increments of alkali. An initial portion or section of the curve has steep slopes, and a later portion has relatively flat slopes; between these lies an intermediate section in which the slope changes from high to low; this intermediate part represents the break in the pH curve. At the break in the curve, the rate of decrease in the slope is usually large, about two or more times greater than in the slope at higher pH values.

The break in the pH titration curve of a particular clay serves as a control point by indicating the amount of alkaline material that should be added to the clay. If the clay, as previously indicated, is adjusted with proper alkaline material (usually sodium carbonate) to the pH approximating this break, (1) it will become more plastic, (2) it will have a more closely packed body, (3) it will require less mixing water, and (4) it will pass through a brick die more easily. As a result of the pH adjustment, (1) lamination difficulties may be minimized, (2) the formed ware will have greater dry strength although it may require more time or heat for drying, (3) the strength of the fired ware will be greater, (4) the moisture absorption will be lower, and (5) the color, usually, will be brighter.

III. Clays Giving Type-A Curve

Many of the clays which have been tested give the type-*A* titration curve, that is, a curve with a sharp break in the slope (Fig. 1). These clays therefore are not difficult to treat because the amount of alkali needed is indicated definitely. Maximum improvement and benefits, moreover, are obtained by adjusting a clay of this type with certain alkaline materials, particularly sodium carbonate, to the pH corresponding to the break in the titration curve of the clay.

Why the break in the titration curve corresponds to the favorable point of treatment is a question which may well be asked. The results of preliminary tests indicate that preceding this break a high percentage of the sodium added enters the base-exchange material, whereas beyond this break the percentage falls off rapidly. Because the benefits obtained arise largely from the properties given to the clay by a considerable saturation of the base-exchange material with sodium, these results help to answer this question. It should be stated, furthermore, that beyond the point of rapid absorption of sodium by the base-exchange material,

sodium carbonate, as such, accumulates rapidly and tends to cause undesirable granulation as does an accumulation of any other soluble salt or electrolyte. The region beyond the break is thus one of diminishing returns as to benefits.

IV. Clays Giving Type-B Curve

The type-*B* curve obtained with certain clays varies considerably, and it is often difficult to determine the point on the curve which represents the best treatment because two or more breaks may occur in the curve. A recent case of this kind encountered at a plant test is exemplified by curve *B* in Fig. 2. There are two breaks in the curve, and with no further information, there might be some question of whether to select the lower or upper break as the point of treatment. The fact that the lower break falls in the acid range and that the correct point of treatment normally falls in the alkaline range suggests the selection of the upper break. The quality of specimens produced in laboratory tests has confirmed the selection of the upper break as the favorable point of treatment.

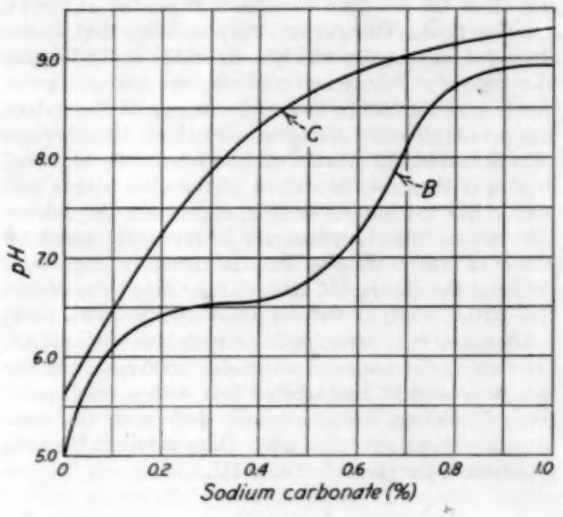

FIG. 2.

Because the lower portion of the curve somewhat resembles that obtained on titrating a soluble aluminum salt with an alkali,[3] it was thought that easily soluble aluminum compounds might be present in the clay. A sample of the clay was carefully leached with calcium chloride solution to remove the easily soluble aluminum. (On leaching an acid clay with a calcium chloride solution, some hydrochloric acid is formed by exchange reactions and any soluble aluminum present is removed as the chloride.) The clay was then titrated with a solution of sodium carbonate, and the resulting pH values were plotted against added alkali to give curve *C* in Fig. 2. It is apparent that the lower break is now absent, and a smooth curve, similar to that of type *A*, is obtained. It is concluded, therefore, that soluble aluminum compounds may be one cause of the double breaks which sometimes occur in the titration curves.

The aluminum involved in these reactions may exist either as a soluble compound in the clay or it may be liberated in soluble form by base-exchange reactions. Because of the relatively large quantity of sodium carbonate consumed in the reaction, however, it is believed that the aluminum exists at least partially in soluble form. This fact was substantiated further by the behavior of another clay of the same type. This clay was titrated as removed from the clay bank without previous drying and the type-*B* curve was obtained; when this same clay, however, was formed into brick, passed through the plant drier, and tested, a smooth type-*C* curve resulted. The explanation for this result may be that the heat in the drier dehydrated the soluble aluminum hydroxide or broke up the soluble aluminum salt; in either case the aluminum compounds were changed to a compound which no longer reacted readily with the sodium carbonate.

The dip or first break in the type-*B* curve is often associated with the presence of soluble salts. Whenever soluble sulfates are present in quantities of at least 1000 p.p.m., this break in the curve usually is noticeable and it is often quite pronounced. If these soluble salts are inactivated by the addition of a barium compound which forms insoluble products and sodium carbonate is then added to the clay, the resulting pH curve assumes the regular *A* type. This is illustrated by the curves in Fig. 3 (*B*, before the addition of barium carbonate; *A*, after).

In the experimental work in the laboratory, it was found that the *B*-type curve was characteristic of acid clays containing soluble aluminum, for example; the sandy, yellow clays from the southeastern part of the United States. These clays also usually contain a small quantity of micaceous material, but the influence of this material on the type of curve obtained is not known. It now appears that the type-*B* curve is essentially either the *A* or *C* type which has been somewhat deformed because of the conditions mentioned.

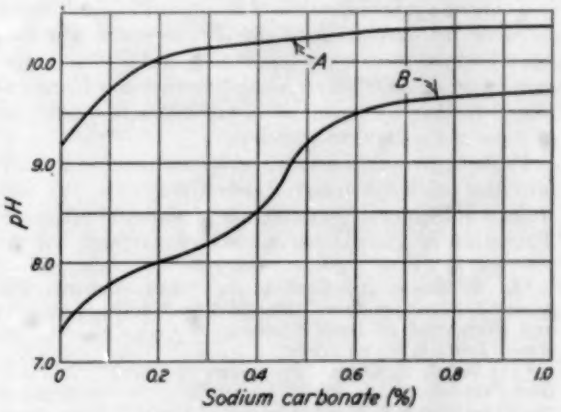

FIG. 3.

[3] H. T. S. Britton, Hydrogen Ions, p. 258. D. Van Nostrand Co., Inc., New York, 1929; *Ceram. Abs.*, 9 [1] 68 (1930).

V. Clays Giving Type-C Curve

Clays giving the *C*-type curve are encountered occasionally. Because these clays usually are acid, they require the addition of rather large amounts of sodium carbonate to neutralize the acidity and to produce the final break in the curve on the alkaline side. The explanation for the gentle slope without a distinct break may be found in the fact that there is a gradual and marked hydrolysis of the large amount of absorbed sodium introduced in the neutralization of the acidity.

Data concerning two clays which give the *C*-type curve are presented in Table I. These clays contain high amounts of exchangeable hydrogen and considerable amounts of exchangeable calcium and magnesium.

TABLE I

EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY OF TWO CLAYS

Exchangeable cation	M.e./100 gm. of clay	
	Clay No. 101	Clay No. 128
Hydrogen	7.82	3.42
Calcium	4.63	2.60
Magnesium	4.21	5.85
Sodium	0.25	0.31
Potassium	0.36	0.56
Total cations determined	17.27	12.74
Total exchange capacity	18.30	12.90

The amounts of exchangeable magnesium in fact are unusually high, especially when compared to the amounts of exchangeable calcium present, which ordinarily exceed the amounts of magnesium by several fold. These relatively high amounts of exchangeable magnesium may explain, in part, the gradual slope of the curves, inasmuch as Bower and Truog[4] have shown that exchangeable magnesium may be present partially as a basic salt and that in this condition the magnesium is displaced with difficulty.

The nature of the exchange material present in the clay is another factor which may tend to produce the *C*-type curve. Certain evidence indicates that at least two types of exchange material may be present, namely, (1) montmorillonite (characterized by an expanding lattice type of crystal) and (2) hydrous mica, which has a nonexpanding lattice type of crystal.[5] The presence in a clay of a preponderance of montmorillonite appears to favor the derivation of the *A*-type curve whereas, when hydrous mica is predominant in a clay, the *C*-type curve may result. These possibilities are now being explored further by means of X-ray diffraction analysis of some of the clays in question.

Table II gives data relating to the entrance of sodium into the exchange material when clay No. 128 was treated with increasing amounts of sodium carbonate. The break in the pH curve for this clay was not attained until the base-exchange material reached a 75% saturation with sodium. The degree of sodium saturation needed with different clays in general varies from 20 to 75%. Not only must the pH of a clay be properly adjusted as previously explained,[1(b)] but a certain degree of saturation of the clay with sodium must also be attained.

TABLE II

Amount of Na_2CO_3 added to clay No. 128 (%)	Exchangeable sodium present (m.e./100 gm.)	Extent of sodium saturation (%)	Portion of added sodium taken up by exchange material (%)
None	0.31	2.4	
0.1	1.57	12.2	23.8
0.2	3.32	25.8	28.4
0.3	4.96	38.5	29.2
0.6	8.07	62.6	24.1
0.8	9.78	75.7	22.4

Table II shows that with the various additions of sodium carbonate only about 25% of the sodium added has been taken up by the exchange material. This may be due to the presence of a preponderance of the nonexpanding-lattice type of exchange material which does not allow the entrance of sodium as readily as the expanding type. There is also the possibility that intense drying of an acid clay which contains the expanding lattice type of exchange material may cause so much contraction of the lattice that the entrance of the sodium ion (whose effective diameter is relatively large because of high hydration) into the exchange is greatly hindered. If this is the case, treatment of the clay with a substance like calcium hydroxide, containing the calcium ion (whose effective diameter is relatively small because of low hydration and is therefore capable of entering the contracted lattice) may help to re-expand the lattice so that sodium thereafter is more easily again taken up. In accordance with this idea, an acid clay which did not respond readily to the sodium carbonate treatment was treated first with a small quantity of calcium hydroxide and then with the usual amounts of sodium carbonate. Data obtained from this experiment are given in Table III.

TABLE III

Addition (%)		Extent of base-exchange capacity sodium saturated (%)	Portion of sodium added found in exchangeable form (%)	Reaction of clay pH
$Ca(OH)_2$	Na_2CO_3			
None	None	1.35		5.58
None	0.2	5.50	22.6	6.94
0.05	0.2	17.70	89.5	7.09

These data show that the addition of a small amount of calcium hydroxide has greatly favored the subsequent absorption of sodium by the exchange material. Verification of this favorable action will have to await further experimentation. When a clay becomes rather dry, rewetting and allowing to stand in a wet condition for some time often greatly improves its behavior on treatment. This conclusion agrees with the foregoing statement, inasmuch as water alone, given sufficient

[4] C. A. Bower and Emil Truog, "Base-Exchange Capacity Determination as Influenced by Nature of Cations and Formation of Basic-Exchange Salts," *Soil Sci. Soc. Amer. Proc.*, **5**, 86–89 (1941).

[5] (*a*) Ralph E. Grim, "Properties of Clays," *Ill. State. Geol. Surv. Circ.*, No. 49, 30 pp. (1939); (*b*) "Relation of the Constitution to the Properties of Clays," *Jour. Amer. Ceram. Soc.*, **22** [5] 141–51 (1939).

time, apparently tends to re-expand a lattice that has become contracted due to drying.

If the clays being treated are calcareous, favorable action from pretreatment with a small amount of calcium hydroxide is hardly to be expected. The data in Table IV obtained with a calcareous clay, No. 132, which has an exchange capacity of 12.3 m.e. per 100 gm. of clay, confirm this expectation.

These factors, which account for the *C*-type curve, are now being studied by means of various methods including X-ray analysis.

TABLE IV

Treatment with		Exchangeable sodium present (m.e./100 gm.)	Extent of sodium saturation (%)	Portion of added sodium taken up by exchange material (%)
$Ca(OH)_2$ (%)	Na_2CO_3 (%)			
None	None	1.20	9.8	
0.05	None	0.93	7.5	
None	0.30	3.10	25.2	12.4
0.05	0.30	2.74	22.3	9.7

VI. Soluble Salts

Soluble salts are sometimes found in clays being treated. These salts usually do not lessen the benefit from the treatment unless they are present in quantities of at least 500 p.p.m. When soluble salts are present in appreciable quantities in the clay, the fired ware will usually have a so-called kiln scum. This discoloration is more pronounced with an increase in the soluble salt content. When the quantities of soluble salts are low, treatment with sodium carbonate eliminates the kiln scum. Some clays that scum badly when they are fired have a clearer color when they are treated. The sodium carbonate probably reacts with the soluble salts, often largely calcium and magnesium sulfates, forming sodium sulfate and insoluble calcium and magnesium carbonates. When the ware is fired, this sodium sulfate undoubtedly decomposes and reacts with the silica present and forms sodium silicate at the firing temperature. If the quantity of soluble salts is large, an objectionable glazed effect is produced on the surface of the ware.

Under these conditions, the clay should first be treated with a barium compound. In experimental work, the writers have found that clays containing soluble salts up to 500 p.p.m. and even more may be treated successfully with sodium carbonate for improved workability and elimination of scum without the use of barium compounds.

VII. Deairing in Relation to pH Control

Because deairing of clays used in industry is practiced to a considerable extent, experiments were made to compare the beneficial effects of deairing with those obtained by means of the sodium carbonate treatment to control pH and the character of base saturation.

A clay which laminated badly when it was processed was used for one of the tests. The clay was first put through the machine without operating the deairing attachment. Sample specimens of this run were preserved, and the remainder of the clay was then rerun through the machine with the deairing attachment in operation. The deairing made the clay more plastic and workable. Treatment of another batch of clay with both sodium carbonate and deairing made the clay considerably more plastic than deairing alone. The specimens were dried, suspended in water, and subjected to the water-disintegration test. The clay which had not been treated or deaired disintegrated rapidly in water. The specimens that were deaired only also disintegrated rapidly in water and scaled along the planes of lamination. Deairing therefore did not prevent the lamination. The deaired specimens, however, which had been treated previously with sodium carbonate, disintegrated slowly in water and no laminations were apparent in the clay body. Deairing, as is well known, makes clay more plastic, but it generally does not bring about certain of the desirable physical changes in the character of the clay that are effected through the use of sodium carbonate. The authors do not contend that the sodium carbonate treatment will entirely replace deairing, but they wish to point out that the use of sodium carbonate may improve the results attained with deairing.

VIII. Use of Wetting Agents in pH and Character of Base-Saturation Control

In the treatment of clays involving pH and the character of base-saturation control, it is essential that the clay become thoroughly moistened so that the exchange of cations between the added substance and the base-exchange material of the clay may take place; otherwise the cation of the added substance cannot enter even though it is in solution. A continuous film of water must be present for diffusion to take place.

In accordance with this idea, a series of experiments was carried out, using six different wetting agents. A 0.1% solution of the wetting agent was made, and 1000 cc. of this solution were added to 15 lb. of dry clay. The sodium carbonate to be added was mixed dry with the clay before the wetting agent was added. The quantity of water was held constant in all tests. After the test specimens had been formed, the amounts of sodium taken up by the exchange material were determined.

The results of these analyses are given in Table V and show that some of the wetting agents promoted the absorption of sodium by the base-exchange material. Although the efficacy of the various wetting agents varied considerably with this clay, the results were generally disappointing. Even the water-disintegration test gave no evidence of an improvement in the body of the formed ware itself from the use of any of the wetting agents. There was some improvement in the workability of the clay when wetting agents Nos. 3 and 4 were used. These two wetting agents were the most effective in promoting the absorption of sodium, and that is probably the reason for their moderately favorable effect on workability.

Test specimens made with treatments indicated in Table V were fired and then subjected to the moisture absorption test. The results are given in Table VI.

TABLE V

ABSORPTION OF SODIUM WHEN SAMPLES OF CLAY NO. 103 WERE TREATED WITH 0.3% OF Na_2CO_3 AND VARIOUS WETTING AGENTS DESIGNATED BY NUMBERS ONLY

No. of wetting agent added	Exchangeable sodium present (m.e./100 gm.)	Extent of sodium saturation (%)	Portion of added sodium taken up by exchange material (%)
None	3.28	30.3	54.6
1	3.68	33.9	61.6
2	3.64	33.5	60.9
3	4.28	39.5	72.3
4	4.53	41.7	76.5
5	4.00	36.9	67.2
6	2.60	24.0	42.5

TABLE VI

No. of wetting agent added	Moisture absorption: 24-hr. cold soak test (%)	Moisture absorption: 5-hr. boil test (%)
None	6.0	9.8
1	6.2	10.0
2	6.0	10.2
3	5.7	9.5
4	5.7	9.7
5	6.0	10.4
6	6.1	10.2

TABLE VII

DATA ON TREATMENT OF WET AND DRY CLAYS

Na_2CO_3 added (%)	Exchangeable sodium present (m.e./100 gm.)	Extent of sodium saturation (%)	Portion of added sodium taken up by exchange material (%)
	Wet clay		
None	0.2	1.8	
0.3	5.7	52.8	97.5
0.6	8.1	75.0	69.7
	Dry clay		
0.3	3.28	30.3	54.6

These data show that wetting agents Nos. 3 and 4 decreased slightly the absorption of moisture. The general conclusion is that the use of wetting agents in addition to sodium carbonate will not materially improve the body structure of ware made from this particular clay.

The desirability of wetting a clay thoroughly on or before treatment for pH control, however, should not be discounted. In working with clays, as previously mentioned, if the clay is treated with sodium carbonate while it is still wet (as removed from the pit), the degree of sodium saturation that may be attained on treatment is often appreciably greater than when the clay is dried before treatment. This fact is brought out by the data in Table VII, involving treatment of clay No. 103, which has a pH of 4.9 and an exchange capacity of 10.8 m.e. per 100 gm.

IX. Summary

The results of further investigations relating to the improvement of clays through a control process of regulating pH and character of base-exchange saturation are presented. These results may be summarized as follows:

(1) The three types of titration curves previously described and which, by means of breaks in their slopes in the alkaline region, are used to determine the amount of basic material to add in the control process may be resolved into two primary types, inasmuch as the third type is a deformed variation of either of the two primary types. This deformation may be caused by the presence of soluble or easily soluble aluminum compounds or other salts. When these are removed or are inactivated, all of the curves fall into one or the other of the two primary types.

(2) One of the two primary types of curves obtained has a sharp break, which indicates approximately the amount of sodium carbonate or other alkaline material that should be added. The other type, usually associated with acid clays, has a much more gradual slope without a decided break.

(3) Soluble salts do not usually affect the control process of treatment unless they are present in quantities greater than 500 p.p.m. With the smaller amounts of soluble salts, the addition of sodium carbonate in many cases prevents kiln scum. When the soluble salt content goes beyond 500 p.p.m., it is usually advisable to inactivate the salts by the use of barium compounds.

(4) The control process may be used to advantage, in combination with deairing in some cases.

(5) The use of certain wetting agents in addition to the control process did not give marked benefits in the case tried.

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FACTORS INFLUENCING AUTOCLAVE CHEMICAL DURABILITY TESTS OF GLASS CONTAINERS*

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Abstract

To secure reproducible results with the chemical durability test in which distilled water is used as the leaching medium, the distilled water must be prepared with special care because certain impurities, of which copper is the most important, are present in small quantities and exhibit a marked effect on alkalinity values. Other impurities, such as lead, iron, sodium silicate, and sodium carbonate, which may be found occasionally in distilled water, do not have as great an effect as copper on alkalinity values. The temperature at which the leaching is carried out has a much greater effect on the test than the length of the test period.

I. Introduction

The chemical durability test for glass containers, wherein distilled water is used as a leaching medium, has aroused considerable discussion regarding its value. The purpose of this paper is not to contribute to this discussion but to demonstrate the influence of various factors, especially the impurities in the distilled water, on this particular test. Variations in time and temperature of the test period have also been investigated. Careful control of these variables contributes materially to the reproducibility and precision of the test.

II. Procedure

(1) Basic Test Procedure

The bottles to be tested were blown out with clean air, filled to the neck with specially prepared distilled water, and the mouths of the bottles were closed with tin foil. A blank of 400 ml. of the same distilled water was placed in a 500-ml. Pyrex-brand Erlenmeyer flask, and the mouth was covered with tin foil. The samples and blank were heated in an autoclave for one hour at 121°C. (15 lb.) with a 30-minute period to bring up to pressure and a 30-minute period to lower to atmospheric pressure. The bottles and blank were then removed and a 100-ml. aliquot of each was titrated (while still hot) with $N/50$ H_2SO_4, using methyl red indicator.

The sample titer minus the blank titer is a measure of the alkaline material leached from the bottle. The results are reported as milligrams of sodium hydroxide per liter.

(2) Preparation of Distilled Water

The water for these experiments was prepared by redistilling the regular laboratory-distilled water in a Pyrex-brand glass water still. This water was boiled to three fourths of its original volume immediately before use to remove any dissolved gases. The container was connected to air scrubbers containing solutions of sulfuric acid and sodium hydroxide so that the water was not permitted to come in contact with ammonia and carbon dioxide while it was cooling.

An adaptation of the Feigl spot test[1] was used for heavy metals. The reagent consisted of 2 mg. of diphenyl thiocarbazone (dithizone) dissolved in 100 cc. of carbon tetrachloride. In testing for copper, 5 cc. of neutral or weakly ammoniacal test solution in a small glass-stoppered test tube was shaken with $^1/_2$ cc. of the solution of dithizone in carbon tetrachloride. The green color of the reagent changes immediately to yellow-brown or reddish purple in the presence of copper. Diphenyl thiocarbazone with many of the heavy metals forms insoluble colored inner complex salts which may be extracted easily with organic solvents. The copper salt is yellow-brown and is formed in solutions that are neutral, ammoniacal, or contain ammonium salts. When a small amount of a dilute solution of the reagent in carbon tetrachloride is shaken with the test solution, copper may be detected in the presence of large amounts of other heavy metals (except noble metals and mercury). Copper dithizone is formed more readily than the other heavy metal dithizone salts. The concentration limit is 1 to 1,660,000.

This test, primarily used for copper, may also be used for lead according to Feigl.[1] In the presence of considerable amounts of potassium cyanide and sodium potassium tartrate, the dithizone test for lead becomes specific, and the other heavy metals are masked by the addition of these salts.

The hydrogen-ion concentration was measured with the Coleman glass-electrode instrument, and the conductivity was measured by a conductivity bridge.†

All of the distilled water used was tested and was found to be free of metallic impurities. The pH was between 6.0 and 6.5, and the specific conductivity of all water used was not more than 0.2×10^{-6} mhos at 20°C. Distilled water with lower conductivity may be prepared,[2] but it was found that the water used gave reproducible results.

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* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (Glass Division). Received April 1, 1941.

[1] Fritz Feigl, Qualitative Analysis by Spot Tests, p. 46. Nordemann Publishing Co., 215 Fourth Ave., New York, N. Y., 1939.

† Model RC-B manufactured by the Industrial Instrument Co., Jersey City, N. J.

[2] J. Kendall, "Preparation of Conductivity Water," *Jour. Amer. Chem. Soc.*, **38** [11] 2460–66 (1916).

(3) Test for Reproducibility

Nine different 8-oz. flat bottles were used for this test, and a series of five tests was run to determine the reproducibility of the test. The water for each test was prepared separately, and each test was run independently. The results are shown in Table I.

TABLE I

REPRODUCIBILITY OF AUTOCLAVE CHEMICAL DURABILITY TEST*

Bottle	Test 1	Test 2	Test 3	Test 4	Test 5	Avg.
	Sodium hydroxide (mg./l.)					
A	4.8	6.0	5.2	5.2	5.6	5.4
B	6.8	6.8	6.8	5.6	6.4	6.5
C	8.8	8.8	9.2	7.2	10.0	8.8
D	10.0	8.4	9.6	9.6	10.8	9.7
E	7.6	9.6	8.8	8.8	10.0	9.0
F	12.4	14.4	14.4	14.0	16.4	14.3
G	18.8	17.4	16.8	15.2	18.4	17.3
H	26.0	22.8	23.6	22.4		23.7
I	31.6†	30.8†	34.8†	37.2†	36.0†	34.1†

* The distilled water for each test was prepared separately, and each test was run independently.
† Indicates flaking.

(4) Effect of Copper

Nine bottles of the same type and size as those used for the reproducibility test were taken for this test. The distilled water was prepared as in the first test, and just before it was poured into the bottles a measured amount of copper sulfate solution was added.

Tests were run at seven different concentrations of copper, namely, 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, and 3.0 p.p.m. of copper ion. The tests were run in duplicate, and the results were averaged. The amount of copper added to the water was the only variation in the test. The data from this experiment are summarized in Table II.

The conductivities of distilled water containing different concentrations of copper ion were measured. After the total alkaline material was titrated, another portion of the solution in each bottle was cooled to 20°C., and the conductivity was measured. The data obtained by this experiment are given in Table III.

TABLE II

EFFECT OF COPPER ON AUTOCLAVE CHEMICAL DURABILITY TEST

	Copper (p.p.m.) added to distilled water							
	None	0.1	0.2	0.5	1.0	1.5	2.0	3.0
Bottle	Sodium hydroxide (mg./l.)							
A	5.4	3.2	2.4	1.6	1.6	0.4	0.4	0.4
B	6.5	4.8	3.6	3.6	3.6	2.4	1.2	0.0
C	8.8	7.6	6.4	8.4	7.6	6.4	4.4	1.2
D	9.7	8.4	7.6	9.6	7.2	7.2	6.8	3.2
E	9.0	7.2	6.8	8.4	7.2	6.4	4.8	2.0
F	14.3	11.2	12.4	10.4	12.0	14.0	13.6	7.6
G	17.3	16.4	14.8	13.6	14.4	14.8	14.8	14.8
H	23.7	28.4	27.6	28.4	26.4	21.2	20.0	16.0
I	34.1*	11.6*	11.6	5.2	20.0*	12.4*	10.8	4.8

* Indicates flaking.

TABLE III

EFFECT OF COPPER ON CONDUCTIVITY*

	Copper (p.p.m.) added to distilled water							
	None	0.1	0.2	0.5	1.0	1.5	2.0	3.0
Bottle	(Reciprocal ohms at 20°C.) × 10^{-6}							
†	0.2	0.3	0.3	0.3	0.5	0.7	0.9	1.2
A	1.8	1.7	1.4	3.4	7.1	1.4	1.9	1.5
B	2.0	1.7	1.5	1.9	1.8	1.7	1.7	1.7
C	2.8	2.2	2.3	2.6	2.7	2.8	2.6	1.9
D	3.0	2.2	2.7	2.8	2.6	2.9	3.4	2.6
E	2.8	2.1	2.1	2.7	2.6	2.7	2.6	2.6
F	7.7	3.0	3.2	5.0	5.4	6.0	4.5	5.4
G	7.0	4.7	3.8	3.8	4.8	6.4	5.1	3.3
H	8.2	7.1	6.4	7.3	8.8	5.1	6.9	3.7
I	9.2	3.0	2.6	5.9	5.9	4.5	4.2	2.7

* Measurements obtained from same solutions used to obtain values for Table II.
† Conductivity of distilled water before autoclaving.

(5) Effect of Other Ions

A procedure, identical to that in the preceding experiment, was used to determine the effects of the addition of small amounts of sodium carbonate, sodium silicate, lead acetate, and ferrous sulfate to the distilled water. These salts, prepared as already outlined, were added to the distilled water in amounts of 4 and 8 p.p.m. Samples were used from the same lots of bottles that were used in the previous tests.

TABLE IV

EFFECT OF VARIOUS SALTS

	Salts or metal ions (p.p.m.) added to distilled water								
		Na_2CO_3		Na_2SiO_3		Lead		Iron	
	None	4	8	4	8	4	8	4	8
Bottle	Sodium hydroxide (mg./l.)								
A	5.4	6.0	7.2	7.6	7.6	8.4	6.8	2.0	2.8
B	6.5	7.2	8.4	7.6	8.8	8.4	7.6	4.0	5.2
C	8.8	8.8	10.4	10.4	10.4	10.8	9.2	7.6	5.6
D	9.7	10.4	10.4	10.8	10.8	10.8	10.0	7.6	6.0
E	9.0	12.8	11.6	11.6	10.8	10.0	8.4	8.4	5.6
F	14.3	18.4	17.6	16.4	18.0	14.0	12.8	14.0	11.0
G	17.3	18.4	19.2	19.2	20.0	14.8	13.2	16.4	15.6
H	23.7	24.4	26.4	29.6	26.8	21.6	19.2	25.2	23.6
I	34.1	38.4*	39.2*	41.6*	45.2*	35.2*	22.0*	16.8	12.0

* Indicates flaking.

In the ferrous-sulfate test series, the blank run simultaneously with the bottles was acidic to methyl red. In the reported results, the amount of sodium hydroxide required to neutralize 100 ml. of the blank was added to the amount of the alkali extracted from the bottles, which was determined by titration with $N/50$ acid. These data are given in Table IV.

The conductivities of the distilled water containing the different amounts of the salts were determined on the solutions left in each bottle after the total alkaline material was found by titration. These data are given in Table V.

(6) Effect of Time and Temperature

The basic one-hour test period was extended for this study to 2, 3, 4, and 5 hours, and, in addition to the 121°C. basic-test temperature, tests were run at 60°, 75°, 90°, and 105°C.

The test at 105°C. was run in an autoclave, as described in the basic test, except for the variation in temperature. The tests at 60°, 75°, and 90°C. were run in a constant-temperature water bath. For the tests in the water bath, the distilled water was heated to the test temperature and poured into the bottles, which were immediately placed in a water bath already at the test temperature. Aliquots of 100 ml. were titrated as soon as the bottles were removed from the water bath.

Table VI contains the data obtained in this experiment, grouped with the temperature constant. Table VII contains the same data, grouped with the time constant.

TABLE V

EFFECT OF VARIOUS SALTS ON TEST CONDUCTIVITY*

	Salt or metal ions (p.p.m.) added to distilled water								
		Na_2CO_3		Na_2SiO_3		Lead		Iron	
	None	4	8	4	8	4	8	4	8
Bottle	(Reciprocal ohms at 20°C.) × 10^{-4}								
	0.2	1.6	1.9	0.5	0.9	0.4	0.6	1.0	1.6
A	1.8	2.8	3.7	3.1	3.8	2.7	2.3	1.4	2.3
B	2.0	3.1	3.9	3.2	3.7	2.7	2.4	1.6	1.8
C	2.8	3.4	4.6	4.1	4.3	3.3	2.9	2.5	2.2
D	3.0	3.8	4.6	4.2	4.4	3.5	2.9	2.7	2.5
E	2.8	4.2	4.7	4.0	4.6	3.1	2.7	2.6	2.9
F	7.7	5.5	6.0	4.9	5.7	3.8	3.4	3.9	3.4
G	7.0	6.2	6.8	5.9	5.9	4.5	4.0	5.1	4.2
H	8.2	7.1	8.2	8.3	8.9	8.5	5.7	7.1	6.7
I	9.2	10.0	12.0	10.4	11.6	8.9	8.4	5.1	3.7

* Measurements obtained from same solutions used to obtain values for Table IV.

† Conductivity of distilled water before autoclaving.

TABLE VI

EFFECT OF VARYING EXTRACTION TIME ON CHEMICAL DURABILITY

No. of hr.	Bottle								
	A	B	C	D	E	F	G	H	I
	Sodium hydroxide (mg./l.)								
	At 60°C.								
1	0.4	0.6	1.0	1.2	0.6	1.2	1.6	3.6	2.0
2	0.4	0.6	1.2	1.2	1.0	1.4	1.8	3.7	2.4
3	0.3	1.0	1.2	1.2	1.1	1.7	2.0	5.1	2.8
4	0.5	0.8	1.5	1.5	1.6	2.2	3.0	5.9	3.6
5	0.6	1.0	1.5	1.6	1.7	2.5	3.4	6.7	4.2
	At 75°C.								
1	0.72	1.0	1.3	1.4	1.6	1.9	2.6	6.2	3.2
2	1.0	1.2	1.6	1.9	1.7	2.2	3.6	7.6	4.1
3	1.2	1.2	2.4	2.4	2.4	2.8	3.6	7.6	4.4
4	1.2	1.8	2.4	2.8	2.4	2.8	3.6	7.6	4.4
5	1.2	1.8	3.0	4.0	2.1	3.1	5.2	8.5	6.0
	At 90°C.								
1	1.6	1.8	2.2	2.6	2.8	3.4	5.2	11.3	3.8
2	1.8	2.0	3.2	3.6	3.0	3.9	5.8	13.4	4.6
3	3.0	3.4	4.9	5.0	4.4	5.2	8.8	15.1	9.2
4	3.1	3.8	5.6	5.6	5.4	7.4	9.7	15.2	11.2
5	3.9	4.0	5.9	6.3	6.0	8.9	10.3	18.4	12.9
	At 105°C.								
1	2.8	3.6	4.4	4.8	4.8	6.7	9.2	14.2	9.2
2	4.6	5.6	7.6	7.6	8.2	11.3	13.8	19.7	15.6
3	5.4	7.6	9.8	11.6	11.2	14.6	19.2	34.3	34.8*
4	6.2	8.3	10.3	11.6	11.6	18.3	20.4	36.6	44.4*
5	8.1	9.7	12.5	14.6	13.4	19.2	22.8	39.2	46.2*
	At 121°C.								
1	5.4	6.5	8.8	9.7	9.0	14.3	17.3	23.7	34.1*
2	10.0	11.2	12.8	15.6	14.0	24.4	26.8	38.3	82.6*
3	13.7	15.6	20.2*	25.1*	18.6	33.1	42.9	55.0*	112.4*
4	14.2*	17.5	21.6*	26.4*	20.2	36.2	43.8	55.4*	113.4*
5	24.4*	26.6*	28.4*	31.6*	27.1	40.1	51.4	63.2*	113.2*

* Indicates flaking.

TABLE VII

EFFECT OF VARYING EXTRACTION TEMPERATURE ON CHEMICAL DURABILITY

Temp. (°C.)	Bottle A	B	C	D	E	F	G	H	I
	Sodium hydroxide (mg./l.)								
	1-hr. test								
60	0.4	0.6	1.0	1.2	0.6	1.2	1.6	3.6	2.0
75	0.72	1.0	1.3	1.4	1.6	1.9	2.6	6.2	3.2
90	1.6	1.8	2.2	2.6	2.8	3.4	5.2	11.3	3.8
105	2.8	3.6	4.4	4.8	4.8	6.7	9.2	14.2	9.2
121	5.4	6.5	8.8	9.7	9.0	14.3	17.3	23.7	34.1*
	2-hr. test								
60	0.4	0.6	1.2	1.2	1.0	1.4	1.8	3.7	2.4
75	1.0	1.2	1.6	1.9	1.7	2.2	3.6	7.6	4.4
90	1.8	2.0	3.2	3.6	3.0	3.9	5.8	13.4	4.6
105	4.6	5.6	7.6	7.6	8.2	11.3	13.8	19.7	15.6
121	10.0	11.2	12.8	15.6	14.0	24.4	26.8	38.3	82.6*
	3-hr. test								
60	0.3	1.0	1.2	1.2	1.1	1.7	2.0	5.1	2.8
75	1.2	1.2	2.4	2.8	2.4	2.8	3.6	7.6	4.4
90	3.0	3.4	4.9	5.0	4.4	5.2	8.8	15.1	9.2
105	5.4	7.6	9.8	11.6	11.2	14.6	19.2	34.3	34.8*
121	13.7	15.6	20.2*	25.1*	18.6	33.1	42.9	55.0*	112.4*
	4-hr. test								
60	0.5	0.8	1.5	1.5	1.6	2.2	3.0	5.9	3.6
75	1.2	1.8	2.4	2.8	2.4	2.8	3.6	7.6	4.4
90	3.1	3.8	5.6	5.6	5.4	7.4	9.7	15.2	11.2
105	6.2	8.3	10.3	11.6	11.6	18.3	20.4	36.6	44.4*
121	14.2*	17.5	21.6*	26.4*	20.2	36.2	43.8	55.4*	113.4*
	5-hr. test								
60	0.6	1.0	1.5	1.6	1.7	2.5	3.4	6.7	4.2
75	1.2	1.8	3.0	4.0	2.1	3.1	5.2	8.5	6.0
90	3.9	4.0	5.9	6.3	6.0	8.9	10.3	18.4	12.9
105	8.1	9.7	12.5	14.6	13.4	19.2	22.8	39.2	46.2*
121	24.4*	26.6*	28.4*	31.6*	27.1	40.1	51.4	63.2*	113.2*

* Indicates flaking.

III. Discussion

(1) Effect of Copper

A comparison of the results of these tests with those obtained by using water free from any metallic impurity shows a marked decrease in the alkaline material leached from the bottles by the water containing the copper. This is evident in the test even when only 0.1 p.p.m. of copper was used; with increasing amounts of copper there is a diminishing decrease of the alkalinity. In the case of bottles A and B, which had the lowest alkalinity with distilled water, the results with 2.5 and 3.0 p.p.m. of copper were reduced practically to zero. The results for the first seven bottles and the average drop in alkalinity for successive amounts of copper show that 0.1 p.p.m. of copper causes a drop of 1.74 mg. of NaOH per liter. One p.p.m. of copper causes a drop of 2.5 mg. of NaOH per liter, and 3 p.p.m. of copper cause a drop of 5.98 mg. of NaOH per liter. The presence of copper in the distilled water in every case decreased the amount of alkaline material leached from the bottle. The inhibition of leaching of alkaline material is not constant for a given amount of copper, however, and it varies considerably with different bottles; for example, 3 p.p.m. of copper reduced the alkalinity test results 92% in the case of bottle A, whereas a reduction of only 15% was obtained for bottle G.

The conductivity of the distilled water, as shown in Table III, gradually increases as the amount of copper added is increased. The conductivity of the extract from the bottles generally shows a slight decrease as the amount of copper added to the water is increased. The conductivity measurements, in general, check the trend shown by the titration method, but the change is much less pronounced. Other observers[3] have shown that the titration and conductivity methods agree only when the material leached from the bottle is in solution.

(2) Effect of Other Ions

The average of the results, obtained in the experiments with Na_2CO_3 and Na_2SiO_3, shows that the alkalinity is increased by the presence of small amounts of these salts (Table IV). With Na_2CO_3, the alkalinity increased from 11 to 33% of its original value, and with Na_2SiO_3, the alkalinity increased from 11 to 41% of its

[3] E. H. Hamilton, D. K. Hubbard, and A. N. Finn, "Comparison of Titration and Conductivity Methods for Determining Relative Solubility of Glass," abstracted in *Glass Ind.*, 21 [5] 226 (1940).

original value. Bottles which showed larger increases in alkalinity with Na_2CO_3 also showed larger increases in alkalinity with Na_2SiO_3, and bottles which were attacked slightly with Na_2CO_3 also showed only slight attack with Na_2SiO_3. Only bottle I showed a considerably greater increase in alkalinity with Na_2SiO_3 than with Na_2CO_3. It was to be expected that the addition of these alkaline salts would tend to increase the attack on the glass. Bacon and Burch[4] report that the attack of $N/50$ sodium hydroxide is much more severe than that of distilled water. The increases in alkalinity in most cases were not excessive and were not so large as the errors produced by similar concentrations of copper.

TABLE VIII

RATIO OF ALKALINITY

No. of hr.	Bottle A	B	C	D	E	F	G	H	I	Avg.
	Ratio of tests at 121°C. and at 60°C.									
1	13	11	9	8	15	12	11	7	17	11
2	25	19	10	13	14	17	15	10	34	17
3	45	15	17	21	17	19	21	10	40	23
4	28	22	14	18	12	16	14	9	31	18
5	40	26	19	20	16	16	15	9	29	21
	Total average									18

TABLE IX

RATIO OF ALKALINITY

Test temp. (°C.)	Bottle A	B	C	D	E	F	G	H	I	Avg.
	Ratio of tests at 1 hr. and at 5 hr.									
60	1.5	1.4	1.5	1.3	2.8	2.0	1.9	1.9	2.1	1.8
75	1.5	1.8	2.3	2.8	1.3	1.6	2.0	1.4	2.9	1.9
90	2.4	2.2	2.7	2.4	2.1	2.6	2.0	1.6	3.4	2.3
105	2.9	2.7	2.8	3.0	2.8	2.8	2.5	2.7	5.0	3.0
121	4.5	4.0	3.2	3.2	3.0	2.7	3.0	2.6	3.3	3.4
	Total average									2.5

The results obtained when small amounts of lead acetate were added to the distilled water were not so conclusive as in the case of copper. Bottles G, H, and I were affected most, again showing that the heavy metal ions inhibit leaching of alkaline material to a different extent in different bottles. The ferrous-sulfate additions to the distilled water produced effects somewhat different from those observed with the other salts because of the tendency of the salt to break down on heating and to produce an acidic solution.

(3) Effect of Time and Temperature

The length of time of the test period usually becomes increasingly important with increasing temperature, but certain types of bottles show a considerable increase in alkalinity with increased periods of extraction time even at low temperature (Table VI).

In comparing the results of the tests at high temperature (121°C.) with those at low temperature (60°C.), the ratios of the amount of alkaline material extracted are as follows: 11 to 1 for the 1-hour test; 17 to 1 for the 2-hour test; 23 to 1 for the 3-hour test; 18 to 1 for the 4-hour test; and 21 to 1 for the 5-hour test. For the combined values of all these tests, the ratio is 18 to 1 (see Table VIII).

The ratio of the alkaline material extracted in the 5-hour to 1-hour test is as follows: 1.8 to 1 at 60°C.; 1.9 to 1 at 75°C.; 2.3 to 1 at 90°C.; 3.0 to 1 at 105°C.; and 3.4 to 1 at 121°C. For the combined values of all the 60°, 75°, 90°, 105°, and 121°C. tests, the ratio is 2.5 to 1 (Table IX). Thus it is indicated that of these two factors which influence the results obtained in this test the temperature is the more important.

IV. Conclusions

(1) Copper, the most common impurity in distilled water, has more influence on the chemical durability test than any of the other impurities investigated.

(2) Iron has more effect on alkalinity than lead, but neither iron nor lead affects the alkalinity as much as copper.

(3) Sodium carbonate and sodium silicate impurities in the distilled water slightly increase the attack on the glass.

(4) Conductivity measurements are a satisfactory indicator of the quality of distilled water, but they are unreliable for measuring the chemical durability of glass.

(5) Of the two test conditions, (*a*) the length of time used for the leaching and (*b*) the temperature at which the leaching is carried out, the latter was found to have the greater effect on the alkalinity.

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SEVENTH STREET ROAD
LOUISVILLE, KENTUCKY

[4] F. R. Bacon and O. G. Burch, "Effect of Time and Temperature on Accelerated Chemical Durability Tests Made on Commercial Glass Bottles, II," *Jour. Amer. Ceram. Soc.*, **24** [1] 29–35 (1941).

TESTS FOR THE CHEMICAL DURABILITY OF BOTTLES*

By A. J. Liebmann and M. Rosenblatt

Abstract

(1) A description is given of a reliable and reproducible analytical method for testing the small amount of alkali derived from the glass by titration. (2) The magnitude and type of extraction of various commercial glasses by neutral alcoholic liquids during the accelerated test are determined, and a method of sealing alcoholic liquids in bottles during tests run above the boiling point is described. (3) The conditions of the test are determined for extracting alkali of the same order of magnitude as in (2), with water used as a leaching medium. (4) A correlation of the results on accelerated tests with visible flaking phenomena is presented. (5) The use of a dispersion function, as measured by standard deviation, to judge the results of an accelerated test is indicated.

I. Introduction

The effect of various liquids on the glass containers in which they are stored has been studied extensively during the last two decades. Some of these liquids (such as water and gin) are essentially neutral in character, and the effect of the glass on them is apparently more pronounced than the acidic liquids which represent the majority of commercial bottlings. The reaction of the glass on the liquid obviously is paralleled by a change of the glass surface itself. The "attack" on the container in some cases results in such "corrosion" of the glass surface that particles of glass are detached from the surface area and may be detected in the liquid. This phenomenon is generally described as "flaking."

The term "durability," as applied to this reaction, measures the ability of a glass surface to resist the attack of a liquid medium.

The major part of the literature[1] records the search for a reliable accelerated test for the durability of glass. The problem involves the use of a convenient laboratory method of not more than one day's duration which would parallel the field results extended over a year or longer. A much smaller part of this literature describes methods used for the quantitative measurement of the durability itself. Because the reliability of an accelerated test must be determined almost exclusively from durability measurements, the most important factor in such a study clearly consists in the development of a reliable analytical determination and the evaluation of its results.

The liquids used as extracting media, in general, have been water and aqueous solutions of acids, bases, and salts. It is to be emphasized, as Burch[2] points out, that water represents in fact a basic solution, inasmuch as the first portions of alkali extracted by water from the commercial soda-lime glass will quickly increase the hydroxyl ions of the unbuffered medium, thereby causing a more rapid attack. This cumulative effect parallels the attack by alkali solutions.

(1) Determination of Action of Solutions

The following three methods have been used in the past to determine the action of various solutions on glass:

(*A*) *Powdered Glass:* Investigators are agreed[3] that only the powder method is suited for testing the durability of glass as glass. Surface variations are eliminated by reduction to powder size, and the larger surface of glass available offers a convenient acceleration in the determination. Although early workers found this method acceptable for judging durability, the use of the powder technique for glass containers has been steadily losing ground. This viewpoint is summed up in the A.S.T.M. preliminary report[4] as follows:

> While in some cases there seems to be a rather definite relation between some of the results of the powder method and surface method, it is the opinion of your advisory group that the powder method does not give data that can be used by the consumer in judging the suitability of glass for his particular purpose. Consequently, it is recommended that further work on, or tests by, the powder method be discontinued as far as glass containers are concerned.

(*B*) *Finished Glass:* This method has the advantage of testing the container in the condition and shape in which it is to be used as well as introducing a minimum number of additional factors, thus allowing the data to be more accurately related to the properties of the interior surface of the container.

(*C*) *Polished Plates:* The plate technique[5] has the advantages of ease in the calculation of area and in the reproducibility of experimental conditions. It is decidedly unsuited for container studies, however, because it creates artificial conditions which involve the alteration of the glass surface.

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* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (Glass Division). Received April 2, 1941.

[1] "Bibliography of Literature on Chemical Durability of Glass (1934 to 1939)," *Glass Ind.*, **20** [9] 328–30 (1939); *Ceram. Abs.*, **20** [1] 10 (1941).

[2] F. R. Bacon and O. G. Burch, "Effect of Time and Temperature on Accelerated Chemical Durability Tests Made on Commercial Glass Bottles," *Jour. Amer. Ceram. Soc.*, **23** [1] 1–9 (1940); p. 2.

[3] "Report of Committee on Chemical Durability of Glass," *Bull. Amer. Ceram. Soc.*, **14** [5] 181–84 (1935).

[4] D. E. Sharp, "Chemical Properties of Glass." Report of Subcommittee III, Committee C-14 of A.S.T.M., June 25, 1940 (unpublished data).

[5] (*a*) Violet Dimbleby, "Corrosion of Glass Bottles by Alcoholic Solutions," *Glass Rev.*, **10** [9] 134–37 (1934); *Ceram. Abs.*, **14** [2] 33 (1935).

(*b*) W. Geffcken and E. Berger, "Chemical Stability of Glasses, II," *Glastech. Ber.*, **16** [9] 296–304 (1938); *Ceram. Abs.*, **18** [2] 45 (1939).

Acceleration has been accomplished by raising the temperature to which the container and medium are subjected. This practice may be divided into two classes, namely, (*a*) atmospheric pressure in which the temperature of the test remains below the boiling point of water (75° to 95°C.) and (*b*) greater than atmospheric pressure in which the temperature is above 100°C., requiring an autoclave.

Owing to the severity of the pressure test, special precautions must be taken to prevent minor variations in procedure. Aqueous solutions are invariably used as media in the pressure test.

The conclusions of Bacon and Burch[6] are important in this connection. They state that there is no consistent relation between the autoclave test conducted with distilled water and the resistance of glass to gin.

(2) Determination of Intensity of Attack

Three main methods have been employed to measure the intensity of attack by a liquid on glass containers.

(*A*) *Volumetric:* The alkali extracted from the glass by the medium is generally determined by titration with standard acid, using as indicators (*a*) iodesine,[7] (*b*) phenolphthalein,[7] (*c*) methyl red,[8] (*d*) bromthymol blue,[9] and (*e*) cresol red.[8] The precision of this determination depends on such factors as the volume of solution titrated, the indicator, the normality of acid, the absorbed CO_2, and the amount of alkali being titrated.

(*B*) *Hydrogen-Ion Change of Medium:* This method[10] lacks precision when it is used with unbuffered solutions unless special precautions are taken which do not lend themselves to routine inspections. This method, furthermore, is of little value for alcoholic solutions because the significance of pH for nonaqueous media is doubtful.

(*C*) *Gravimetric:* Bacon and Burch,[6] who have determined the intensity of attack by measuring the solids (both dissolved and insoluble) in the medium, point out that "the total amount of material extracted from a glass surface by an alcoholic solution is not an index of the likelihood of flakes developing therein."

The literature, in general, points to no definite and reliable procedure for testing the durability of glass. The correlations among different media and at various temperature levels are not good, and the conclusions are readily drawn from data and experimental results whose reliability, if known, is not always presented.

A thorough investigation of the subject has been undertaken by the A.S.T.M., and the Committee report[4] appropriately emphasizes its primary aim as "testing the reproducibility and reliability of various procedures for the measurement of chemical durability by accelerated methods."

(3) Fundamental Nature of Problem

The questions raised in this report are of such fundamental nature that some of them that are related to the present work will be outlined here.

(*A*) *Lyle's Generalization*[4]: "The relative performance of glasses in service may be predicted by an accelerated chemical durability test only if the amount of the chemical attack by the accelerated test is approximately equal to the amount of the chemical attack experienced in service.

"Conversely, the relative performance in service is not necessarily predicted by an accelerated test which produces a chemical attack, the magnitude of which is substantially greater or less than is experienced in service."

(*B*) *Empirical Nature of Problem*[4]: "It is recognized that no one method can be expected to be applicable to all types of glass and that it might be necessary to have more than one and possibly several different methods of test, each applicable for certain specific uses of the product."

The arbitrary use of convenient media to test durability is open to criticism at this stage of the development of the subject. (It will be shown later, for example, that the attempt to substitute neutral alcohol for gin as a leaching medium will not yield good correlation.)

(*C*) *Details of Test*[4]: "Tests of typical methods, 1A and 1B, 11A and 11B, and 111A and 111B, indicate that consistent results can be obtained when directions for the tests are sufficiently detailed and rigidly followed."

The directions for the accelerated test must be rigidly outlined as well as those for the analytical determination in order to yield reproducible results.

(*D*) *Method of Titration*[11]: Finn recommends that (*a*) "direct titrations be dispensed with, except possibly for routine plant control" and (*b*) "back titrations become the official procedure, using as the indicator either the glass electrode, phenol red, bromthymol blue, methyl red, chlorphenol red, or paranitrophenol."

For the precision required by alcoholic extractions, these observations were essential.

II. Object of Test

Owing to the empirical nature of the problem of durability, the basic criterion of the present study has been to retain in the accelerated procedure as many of the characteristics of the field conditions as possible. Because the behavior of gin in commercial glass containers was the immediate problem to be studied, the primary leaching medium chosen was 90-proof (45% ethyl alcohol by volume) gin. The bottles chosen for the test, furthermore, were those actually made for

[6] F. R. Bacon and O. G. Burch, "Resistance of Bottles to Neutral Alcoholic Solutions," *Jour. Amer. Ceram. Soc.*, **23** [5] 147–51 (1940).

[7] Alix Cornille, "Chemical Resistance of Glasses," *Céram., Verrerie, Émail.*, **4** [1] 11–15 (1936); *Ceram. Abs.*, **16** [8] 239 (1937).

[8] A. K. Lyle, William Horak, and D. E. Sharp, "Effect of Alumina on Chemical Durability of Sand-Soda Lime Glasses," *Jour. Amer. Ceram. Soc.*, **19** [5] 142–47 (1936).

[9] W. E. S. Turner, *et al.*, "Basis of a Standard Test for Chemical Durability of Glass Bottles," *Jour. Soc. Glass Tech.*, **19**, 171–88 (1935); *Ceram. Abs.*, **16** [7] 200 (1937).

[10] L. F. Gabel, "Free Alkali in Glass," *Jour. Amer. Pharm. Assn.*, **23** [12] 1174–77 (1934); *Ceram. Abs.*, **14** [9] 212 (1935).

[11] D. E. Sharp, *loc. cit.*, Appendix C (see footnote 4).

production, and they were used without any modification of shape or internal surface.

The present studies involve the method and technique of the accelerated test, the reliability of the determination of the degree of attack on the glass, and the application of this procedure to several commercial glass bottles.

The data obtained were analyzed by statistical methods, and the following factors were investigated:

(1) The distribution (spread) of the data for any set of samples as a measure of the homogeneity of the set within a given range.

(2) The "ranking" of different types of bottles by an examination of the data for significant differences.

(3) The possibility of substituting other, more convenient media (neutral aqueous ethyl alcohol solutions and water) for gin by quantitative measurements of the correlation among media.

(4) The correlation between the analytical data and physical behavior.

(5) The use of the distribution function and the possible effect of sample size in setting up specifications for durability.

III. Method and Apparatus

(1) The Accelerated Test

(*A*) *Containers:* The bottles used in these tests were exclusively pint size and were derived from molds with a screw-top finish at the opening. They were chosen at random from current production of the various glass companies or from current shipments to the plant. Any set of bottles chosen at any one time from one particular source was generally assumed to be homogeneous with respect to their durability. That this assumption is not always valid will be indicated later.

(*B*) *Medium:* (i) Tap water singly distilled from a Barnstead block-tin still was used for the water tests and as a reducing agent in lowering the proof of gin and neutral ethyl alcohol. The distillate was received hot (above 90°C.) into 4-liter Pyrex-brand glass containers protected with soda-lime tubes. The water was then permitted to cool in the CO_2-protected containers and thereafter used at will. The pH of the water should be not less than 5.7 (glass electrode). (ii) For the aqueous alcohol solution, 95% neutral ethyl alcohol was reduced to 45%±0.1% by volume with the water described in (i) just before the test. (iii) A typical gin at an alcoholic concentration of 75% by volume was reduced to 45%±0.1% by volume, just before the test, with the water described in (i).

(*C*) *Rinsing:* The containers must be rinsed thoroughly and uniformly. Each bottle was rinsed twice with hot tap water (approximately 50°C.), twice with distilled water, and once with the extracting medium. Between each rinsing with similar liquids, the bottles were drained for 5 to 10 minutes; between washings with different liquids, they were drained for 15 to 20 minutes. No definite amount of wash liquid was observed, but the liquid was shaken well several times in the bottles before they were drained.

(*D*) *Filling:* The leaching medium (425 ml.) was measured carefully by the dispensing burette into the prepared containers and a 50-ml. head-space was allowed for expansion.

(*E*) *Sealing:* Because the accelerated tests were run at 90°C. and the boiling point of the alcoholic solutions was about 78°C., considerable difficulty was encountered in sealing the commercial bottles. A simple and satisfactory procedure was evolved after a number of trials. A flanged cylindrical cork, the end of which was slightly tapered, was used as a primary sealing agent. The cylindrical diameter of the cork was about $^1/_{16}$ in. greater than the bottle opening, and the end of the tapered portion was about $^1/_{16}$ in. smaller than the bottle opening. The specifications for the cork as used in these tests were as follows:

> Flanged cork, $1^1/_4$ in. long, $^3/_8$ in. flange, $^7/_8$ in. shank. Flange diameter, $1^1/_{16}$ in.; straight shank $^{13}/_{16}$ in. diameter; curved taper for $^1/_4$ in. taking a diameter of $^{13}/_{16}$ to $^{11}/_{16}$ in.

To prevent contamination of the solution, the cork was covered with aluminum foil (0.0008 in. thick), which was folded over the cork to give as smooth a surface as possible. The foil was then pulled partly away from the cork at the bottom to form a small sac. The covered cork was inserted into the bottle and pressed into the opening under gradual vertical pressure on the flange top together with a twisting motion. (The cork will carry the foil with it or, the foil gripping the bottle, the cork will move into the sac of foil without tearing the latter.) The flange and excess foil were cut off smoothly so that the cork was flush with the opening, and the bottle was sealed with a tinned screw cap having a tin-foil liner. The sealing of each bottle can be accomplished within 30 to 45 seconds. The cork seals the bottle, and the cap holds the cork in place. If the cork alone does not give a perfect seal, it offers sufficient primary resistance to vapor flow so that a considerable pressure drop occurs in by-passing the cork, and the screw cap in this case is the ultimate sealing agent.

For the complete sealing procedure, the filled bottle was loosely capped with a screw cap, which has a tin-foil liner, and was placed in a water bath at 50°C. The bath temperature was brought to 70°C. in not less than 30 and not more than 45 minutes and maintained at 70°C. for 5 minutes. The bottles were removed one at a time from the bath and sealed with the aluminum-foil covered corks and screw caps. Each bottle was replaced as quickly as possible into the water bath to minimize the temperature drop. In the tests where water was used as a leaching medium, the screw cap was sufficient to create a seal, and the cork closure was unnecessary.

(*F*) *Accelerated Testing:* The water bath consisted of a $^1/_{16}$-in. stainless steel tank (3 by 2 by $1^1/_2$ ft. in size) with threaded holes conveniently located in the sides for an L-thermometer, two 1500-watt immersion heaters, two drains, a thermoregulator, and openings for the cooling coil. A circulating pump* with a capacity of $^3/_4$ to 1 gallon per minute was clamped to a

* American Instrument Co., Silver Springs, Md.

corner of the bath. The thermoregulator consisted of a bimetallic thermoswitch,† which actuated a relay operating the immersion heaters in parallel. The thermoswitch could be adjusted by means of a screw to any constant temperature position between 15° and 100°C. The walls of the bath and the cover were completely insulated by 1/4-in. transite. Two 1/2-in. holes in the cover were used for automatic feeding of the water by gravity from a reservoir that maintained constant level.

During a 24-hour test run at an operating temperature of 90°C., the variation in temperature at the fixed thermometer was less than 0.25°C., and the variation in temperature throughout the bath at any instant was less than 0.1°C.

After the sealing at 70°C., the temperature of the bath was raised to 90°C. in not less than 50 and not more than 75 minutes. The temperature was maintained at 90° ± 0.25°C. for the desired time.

(*G*) *Cooling:* The bath was cooled rapidly to 71°C. by circulating cold water through the cooling coil, and the bottles were removed singly from the bath at 71°C. As each bottle was removed, the cap was unscrewed and the cork was drawn to prevent "sucking back." The bottle was then recapped with a new cap and cooled to 25°C. by replacing it in the water bath with the thermoregulator set for 25°C.

(2) Determination of Intensity of Attack

Of the methods available for measuring the intensity of attack on glass by a leaching medium, the customary titration of the alkali derived from the glass was chosen as a criterion. The theoretical justification for this choice is obscure.

The mechanism of attack has been considered to be a cumulative weakening of the structure of the glass surface by gradual dissolution of the alkali oxides, followed by the "flaking" of the insoluble oxides. Experimental evidence indicates that "flaking" is accompanied invariably by a rise of pH of the attacking medium. That this relationship is quantitative, however, has yet to be shown.

The titration of the dissolved alkali appears superior to the other methods available from the viewpoint of comparative precision and of significance with relation to alcoholic media.

The amount of alkali, expressed as milligrams of NaOH per liter, extracted by alcoholic media from pint-size, commercial glass containers rarely exceeds 15 mg. per liter. The usual titration technique, therefore, is apparently inadequate. As reported by the A.S.T.M.,[12] the alkali extracted by distilled water from seven commercial glass containers ranged from 7 to 38 mg. per liter (at 95°C. for 24 hr.) or from 31 to 110 mg. per liter (at 130°C. for 5 hr.).

The titration process is outlined as follows: "In the case of the bottles containing water, titrate the total contents and washings of each bottle with *N*/20 HCl using methyl red indicator." Under the autoclave directions where the same titration technique is outlined, the statement is made "check results should not vary by more than 10 mg. . . . " Alcoholic solutions, in many cases, will extract considerably less than 10 mg. of NaOH per liter. A titration technique that would yield check results, under these conditions, within 0.1 mg of NaOH or better was needed.

In a study of the factors affecting the titration of small amounts of NaOH (0.8 to 10.0 mg. per l.) in alcoholic solution, a satisfactory method was attained by the proper refinement of the technique.

The precision was relatively poor until the following factors were standardized: (1) the concentration of NaOH to be titrated, (2) the volume to be titrated, (3) the concentration of the standard titrating solution, (4) the temperature of reaction during titration, (5) the indicator, (6) the aqueous or alcoholic medium (for end point), (7) the direct titration of alkali or back titration, and (8) the constancy and type of light used to note the end point.

(*A*) *Procedure for Titration:* The bottle and its contents at 25°C. were well shaken, and the volume (of the water) was measured in a graduated cylinder. In the case of alcoholic solutions, the percentage of alcohol was determined by a hydrometer. A pipette was used to withdraw 250 ml. of the solution, which were transferred to a distilling flask, the flat bottom portion of which is small in diameter; 25 ml. of approximately 0.01*N* H_2SO_4 were added by burette, followed by a few crystals of silicon carbide. The flask was attached to a distillation unit with a 6-in. still-head (all standard taper ground-glass joints were used). The contents were distilled into a graduated receiver until 250 ml. of distillate were collected. The flask was then removed after a slight rinsing of the still-head, and was heated to boiling on a hot-plate, care being taken to avoid spattering. Four drops of a 0.04% solution of bromthymol-blue indicator (prepared according to Clark) were added, and the solution was titrated hot with 0.01*N* NaOH to a blue end point. A blank of the original leaching medium, stored in Pyrex-brand glass, was titrated at the same time.

The end point was taken as the first appearance of a definite blue in the green solution. If the solution cools during titration, it should be reheated to boiling before the end point is reached, that is, while the solution is still distinctly yellow. It was found necessary to judge the end point under the constant artificial light environment of a fluorescent light background; difficulty may be encountered in duplicating this end point in dim daylight or by incandescent electric light.

A knowledge of the exact normality of the sulfuric acid to be added in excess is unnecessary, provided the volume added to the unknown is identical with that added to the blank. The amount of alkali extracted from the container by the medium, expressed in NaOH (mg. per liter), is as follows:

$$X = \frac{1000}{V_s} \cdot 40 \cdot N \, (V_b - V_s).$$

Where V_s = titration medium volume (ml.).
N = standard alkali normality.
V_b = standard alkali volume in back-titrating blank (ml.).
V_s = standard alkali volume in back-titrating sample after accelerated test (ml.).

† Fenwall, Inc., Ashland, Mass.

[12] D. E. Sharp, *loc. cit.*, Appendix B (see footnote 4).

The precision attainable over a range of alkali content from 1 to 10 mg. of NaOH per liter and for an acid excess, ranging from 10 to 30 ml. of 0.01*N* H_2SO_4, is quite constant, $\sigma = 0.01$ mg. per liter.

The total time involved to run a complete test (from the preparation of the media to the final titration) on 24 bottles, using water, alcohol, and gin as leaching agents, was 48 hours. In examining as few as 2 to 6 bottles, the test can be started in the morning and the results will be completed the following afternoon.

IV. Results

Ten batches of bottles were obtained from various glass-container manufacturers throughout the country. Each batch consisted of 24 bottles, chosen at random by the manufacturer during one day of production. The 240 bottles were received in December, 1940, and the analyses were completed on all within two months. They were exclusively of pint size and flask-shaped, similar to the containers usually used for gin. The small variation in internal surface area due to difference in shape was neglected.

The chemical composition of the glasses, representative of normal soda-lime commercial containers, is as follows: alkali oxides 13.9 to 16.2%, dibasic oxides 9.5 to 12.5%, alumina 0.4 to 3.0%, and boric oxide 0.0 to 0.8%.

Table I gives the date of manufacture and identifying code of the ten batches.

Each batch of 24 bottles was subjected to 90° ± 0.25°C. as follows: One set of 8 was filled with 90-proof gin; a second set of 8 was filled with 90-proof ethyl alcohol; and the remaining set of 8 was filled with distilled water; 4 of the bottles filled with water were removed from the 90°C. batch after 6 hours, the remaining 4 bottles containing water were removed after 8 hours, and the 16 bottles containing the gin and alcohol were removed after 24 hours.

(1) Distribution

A summary of the results is outlined in Tables II, III, IV, and V for gin, alcohol, water-6, and water-8, respectively. The functions summarizing the data were calculated from their definitions.[13]

The largest number (N) of bottles in any set during these tests was eight. From a statistical viewpoint, this is a "small sample," and estimations of the characteristics of the universe based on a small sample must be treated with extreme caution. If it is known, or can reasonably be assumed, that the distribution of the quality being examined is normal, or approximately so, the application of certain statistical theorems is possible. In any event, when dealing with small samples, it is essential to ascertain the effect of sampling fluctuations on the significance of the observed differences between averages.[14]

It is interesting, from this viewpoint, to examine the anomalous result obtained in the aqueous extractions for batch No. I-f, where more alkali was leached from the glass during the 6-hour test than during the 8-hour test. Assuming that the bottles examined were chosen at random from a universe which is homogeneous and approximately normally distributed as to durability, it is possible to estimate the probability that the true average $\overline{X}'$ lies within a range of $\overline{X} \pm a\bar{\sigma}$, where $\overline{X}$ is the observed average.[13(c)]

TABLE I

IDENTIFICATION OF BOTTLES

Code No.	Date of manufacture (1940)
I-b	December
I-e	"
I-f	October
II-a	"
II-b	June
III-b	December
IV-a	September
V-a	
VI-a	
VII-a	December

TABLE II

GIN (45% ALCOHOL BY VOL.)

Column (1) batch No.; (2) No. of samples; (3) average (mg./l.); (4) standard deviation corrected (mg./l.); (5) coefficient of variation (%).

Accelerated test: 90°C. for 24 hr.

(1)	(2) (N)	(3) ($\overline{X}$)	(4) ($\bar{\sigma}$)	(5) (V)
II-b	8	2.14	0.14	6.5
III-b	8	2.14	0.22	10.3
II-a	8	2.42	0.13	5.2
I-e	8	2.93	0.39	13.4
I-b	8	2.96	0.15	5.1
IV-a	8	3.56	0.21	5.9
V-a	8	3.61	0.39	10.8
I-f	6	4.97	1.58*	31.9*
VI-a	8	8.18	0.36	4.4
VII-a	6	8.37	0.75	9.0

* Slight leakage occurred in four of the bottles, evidenced by loss in proof (approx. 3° proof).

TABLE III

ETHYL ALCOHOL (45% BY VOL.)

Column (1) batch No.; (2) No. of samples; (3) average (mg./l.); (4) standard deviation corrected (mg./l.); (5) coefficient of variation (%).

Accelerated test: 90°C. for 24 hr.

(1)	(2) (N)	(3) ($\overline{X}$)	(4) ($\bar{\sigma}$)	(5) (V)
II-a	8	3.16	0.42	13.3
II-b	8	3.67	0.28	7.5
III-b	7	5.38	0.59	11.1
I-e	8	5.80	0.22	3.7
IV-a	8	7.53	0.57	7.5
V-a	7	8.48	0.20	2.4
I-b	8	9.82	0.39	4.0
VII-a	8	10.0	0.36	3.6
I-f	8	14.1	0.29	2.1
VI-a	8	16.8	0.30	1.8

[13] (*a*) A.S.T.M. Manual on Presentation of Data, pp. 29–37 (August, 1940).

(*b*) G. U. Yule and M. G. Kendall, Introduction to Theory of Statistics, Chapter XXIII. G. Griffin, London, 1937.

(*c*) $\bar{\sigma}$ (estimated standard deviation of universe corrected for sample size) $= \sigma \cdot \sqrt{\frac{N}{N-1}}$ (see footnote 13(*b*)).

[14] A.S.T.M. Manual on Presentation of Data, Supplement A (August, 1940).

For a P_s of 0.9 and a sample size of 4, a equals 1.360, and the range for I-f in which $\overline{X}'$ could be expected to lie (correct 9 chances in 10) for the 6-hour test is 2.89 to 4.85 mg. per liter and for the 8-hour test is 2.95 to 4.37 mg. per liter.

It is therefore quite possible that the apparent inversion of the average values for the 6-hour and 8-hour aqueous test for batch No. I-f arose from sampling fluctuations.

This discrepancy has been treated at length to emphasize the care required in attempting to draw conclusions which cover a universe based on such small samples as 4, 6, or 8. Discrepancies such as these, furthermore, have been used sometimes to throw doubt on the reliability of a method, whereas an analysis of the dispersion based on the standard deviation might have revealed the fact that the difference was caused by an inherent error in small sampling.

The probability of occurrence of this phenomenon decreases as the sample size increases. One of the fundamental questions to be considered in a study of this kind involves the estimation of sample size to be tested so that this effect is minimized.

Tables II to V indicate that the bottles from the various sources differ not only in the average value of the extracted alkalinity but in the degree of dispersion of this quality as measured by $\bar{\sigma}$. Although two sets of bottles may have comparable mean values, the dispersion of the individual values about the mean may be two to three times greater in one case than the other.

The difference in dispersion among several types of bottles is important in estimating the percentage of bottles that may be defective. For example, the bottles in batches Nos. I-e and I-b (see Table II) may be assumed to have normal durability as measured by the alkali leached from the glass, and the value of 3.40 mg. of NaOH per liter may be assumed to be an upper limit in a specification beyond which it is suspected that the probability of the occurrence of flaking is high. The two averages of the batches are well below this upper limit, and it is probable, on the basis of averages, that No. I-e is superior to No. I-b. Before final judgment can be made, however, it is necessary to know what percentage of bottles in each batch lies above the upper limit.

The difference between the average, $\overline{X}$, and the upper limit in terms of the standard deviation, $\bar{\sigma}$ for No. I-e is 1.2 $\bar{\sigma}$ and for No. I-b is 3 $\bar{\sigma}$.

From the characteristics of the normal curve (2), the range $\overline{X} \pm 1.2\bar{\sigma}$ contains 77% of the members of the batch and $\overline{X} \pm 3\bar{\sigma}$ contains 99.7%.

In the case of No. I-e, therefore, 16.5% of the bottles may be expected to yield values in excess of 3.4 mg. per liter, whereas only 0.15% of the bottles may lie above the upper limit of No. I-b. It is clear that, by a consideration of the dispersion of the values in addition to the mean value, batch No. I-b is far superior to No. I-e.

A critical examination of the assumption of homogeneity of a set to a quality, is important, therefore, because this property is dependent on the dispersion of the values about the mean.[15]

TABLE IV

WATER

Column (1) batch No.; (2) No. of samples; (3) average (mg./l.); (4) standard deviation corrected (mg./l.); (5) coefficient of variation (%).

Accelerated test: 90°C. for 6 hr.

(1)	(2) (N)	(3) ($\overline{X}$)	(4) ($\bar{\sigma}$)	(5) (V)
II-b	4	1.40	0.12	8.9
II-a	4	2.32	0.14	6.1
III-b	4	2.74	0.17	6.3
I-b	4	3.56	0.34	9.6
I-f	4	3.87	0.72*	18.7*
I-e	3	4.14	0.15	3.5
V-a	4	4.33	0.13	3.0
IV-a	4	4.36	0.21	4.9
VII-a	4	7.10	0.22	3.2
VI-a	4	10.56	0.48	4.6

* One sample decidedly out of line; set was not homogeneous.

TABLE V

WATER

Column (1) batch No.; (2) No. of samples; (3) average (mg./l.); (4) standard deviation corrected (mg./l.); (5) coefficient of variation (%).

Accelerated test: 90°C. for 8 hr.

(1)	(2) (N)	(3) ($\overline{X}$)	(4) ($\bar{\sigma}$)	(5) (V)
II-b	4	2.03	0.16	7.8
II-a	4	2.09	0.18	8.8
III-b	4	2.77	0.08	2.7
I-f	4	3.66	0.52	14.2
I-e	4	4.38	0.35	9.3
I-b	4	5.01	0.25	5.0
V-a	4	5.05	0.11	2.3
IV-a	4	5.20	0.22	4.3
VII-a	4	8.31	0.06	0.8
VI-a	4	11.54	0.75	6.5

(2) Ranking

Recent literature on this subject has judged or "ranked" the various types of bottles only on the basis of their average values even though these averages were generally obtained from small sample sets (one set for each average). Table VI demonstrates such a ranking for the ten batches for each of the media. In general,

TABLE VI

COMPARATIVE RANKING BY ALKALI EXTRACTION

Batch	Gin	Alcohol	Water-8	Water-6
II-b	1	2	1	1
III-b	2	3	3	3
II-a	3	1	2	2
I-e	4	4	5	6
I-b	5	7	6	4
IV-a	6	5	8	8
V-a	7	6	7	7
I-f	8	9	4	5
VI-a	9	10	10	10
VII-a	10	8	9	9

[15] (*a*) A.S.T.M. Manual on Presentation of Data, pp. 21–29 (August, 1940).
(*b*) W. A. Shewhart, Economic Control of Quality of Manufactured Product. D. Van Nostrand Co., Inc., New York, 1931.

the ranking is fair; the three top bottle types are the same for each medium, and the three lowest types, with two exceptions, are also identical.

An examination of the four horizontal ranking numbers for each batch reveals the existence of several inversions. Batch No. I-f exhibits an appreciable discrepancy between the aqueous media ranking and that of the alcoholic media; batch No. IV-a exhibits a similar inversion to a lesser degree; and batch No. I-b shows no central tendency relating to rank. The remaining batches, however, indicate a good correlation among the four media.

This method of ranking (based solely on averages of small samples) may be misleading because the dispersion of the individual values about the average may lead to an overlapping of the ranks.

Figure 1 shows the ranking for the 6-hour water test where the average is centered in a range of $6\bar{\sigma}$. With the assumption that the universes are normal, or approximately so, the range $6\bar{\sigma}$ will include at least 95% of the samples.[13(a)]

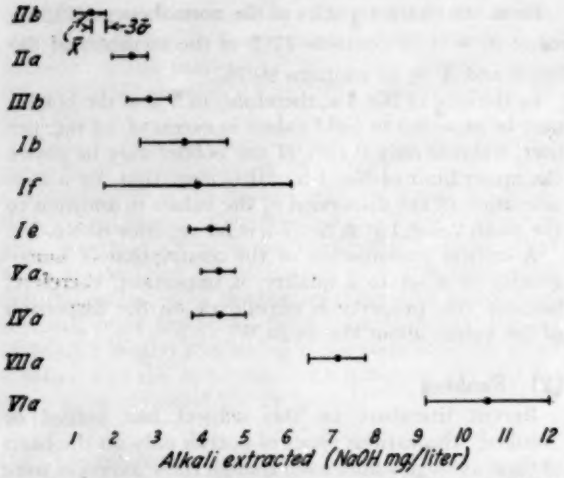

FIG. 1.—Significant differences among average values of alkali extracted by water during a 6-hour accelerated test at 90°C.

It is apparent at once that considerable overlapping occurs among some of the batches and the three inversion batches, Nos. I-f, IV-a, and I-b, are included.

A more delicate measure of the extent to which overlapping occurs is afforded by the use of "Student's *t*-function" to test the significance of the difference between any two means of two small samples.[13(b)] The test is based on a "confidence limit," which sets the dividing line between significant and insignificant differences. A 1% limit was chosen in this case. If the difference between the means of two sets could occur more than 1% of the time, by random sampling both sets were assumed to be derived from the same universe.

Every possible pair of the ten values was examined in this manner for each of the four media and a new ranking was obtained, indicating the apparent or insignificant differences inclosed in a box (Table VII).

TABLE VII

COMPARATIVE RANKING ALKALI EXTRACTION

(With consideration for significant differences)

Rank	Gin	Alcohol	Water-6	Water-8
1	II-b	II-a	II-b	II-b
2	III-b	II-b	II-a	II-a
3	II-a	III-b	III-b	III-b
4	I-e	I-e	I-b	I-f
5	I-b	IV-a	I-f	I-e
6	IV-a	V-a	I-e	I-b
7	V-a	I-b	V-a	V-a
8	I-f	VII-a	IV-a	IV-a
9	VI-a	I-f	VII-a	VII-a
10	VII-a	VI-a	VI-a	VI-a

A re-examination of the three inversion batches shows that, in at least two cases (No. I-f and No. IV-a), the discrepancies were not real. The general "smearing" of ranks occurring in the middle group of the aqueous media implies that ranking is meaningless in that region.

A more realistic classification, based on a sharper division of durability, appears to exist in three defined groups, (1) a top class, Nos. II-b, II-a, and probably III-b; (2) a bottom class, Nos. VI-a, VII-a, and possibly I-f; (3) and an intermediate class containing the remaining batch types. This classification is valid for the four media tested.

(3) Correlation Among Media

Because gin is the "field medium" for this study, it was chosen as the basic type to which the other media were correlated. Table VIII summarizes the average values for the ten batches for each of the four media.

The correlation coefficients[14] are shown at the bottom of Table VIII and afford a quantitative measure of the co-variation of each of the three media with gin.*

The two water tests exhibit a high correlation (perfect correlation is $r = 1.0$) with gin, and they point to the possibility of substituting a simple water-accelerated test of 6 to 8 hours for the more complex 24-hour tests

TABLE VIII

CORRELATION AMONG MEDIA

Average alkali extracted

Batch	(1) Gin (mg./l.)	(2) Alcohol (mg./l.)	(3) Water-6 (mg./l.)	(4) Water-8 (mg./l.)
II-b	2.14	3.67	1.40	2.03
III-b	2.14	5.38	2.74	2.77
II-a	2.42	3.16	2.32	2.09
I-e	2.93	5.80	4.14	4.38
I-b	2.96	9.82	3.56	5.01
IV-a	3.56	7.53	4.36	5.20
V-a	3.61	8.48	4.33	5.05
I-f	4.97	14.1	3.87	3.66
VI-a	8.18	16.8	10.50	11.54
VII-a	8.37	10.0	7.10	8.31

$r_{1,2} = 0.78$. $r_{1,3} = 0.90$. $r_{1,4} = 0.89$.

[14] G. U. Yule and M. G. Kendall, *loc. cit.*, Chapter II.

* The correlation coefficients were also examined for significance and found to differ significantly from $r = 0$ (see also footnote 13(*b*)).

with gin. The alcohol-gin correlation is appreciably lower than those of the water-gin relationships. Owing to the small sample sizes tested, however, it would be advisable to re-examine the alcohol-gin relationship before pronouncing its inferiority to that of water-gin.

A least-squares fit of a straight line was calculated[16] for each pair of correlated media and was drawn for comparison with the observed points (Figs. 2, 3, and 4).

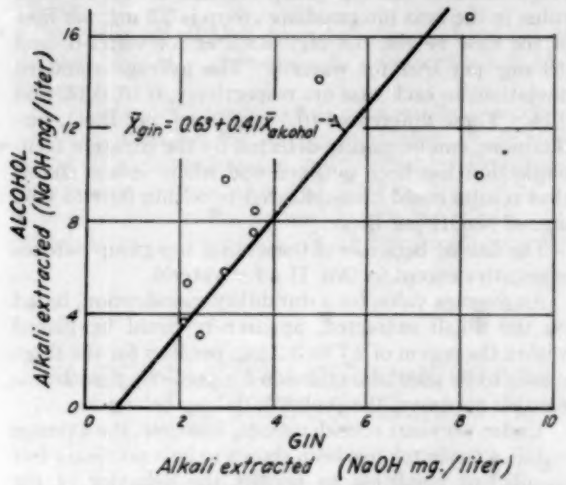

FIG. 2.—Correlation between gin and alcohol with respect to alkali extracted.

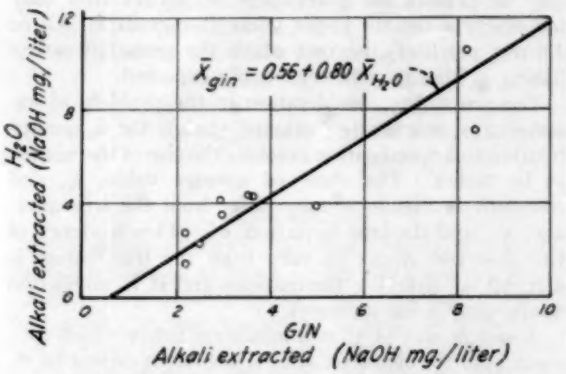

FIG. 3.—Correlation between gin and H_2O-6 with respect to alkali extracted.

The slopes of the regression lines for the three relationships were calculated as follows:

$$b_{\text{gin-H}_2\text{O}}\ (6) = 1.25.$$
$$b_{\text{gin-H}_2\text{O}}\ (8) = 1.41.$$
$$b_{\text{gin-alcohol}} = 2.50.$$

Inasmuch as the units against which all of the media were plotted were identical, NaOH (mg. per liter), the slope of a regression line is a measure of the ratio of the orders of magnitude of the extraction values for the two media. The order of magnitude of the gin extraction obviously agrees best with that of the water-6 extraction and diverges significantly from the alcohol extraction values.

Lyle's principle[4] lays down as a corollary the necessary condition for substitution of media in an accelerated test that the orders of magnitude of the chemical attack (measured by the alkali extraction in this study) for both media be similar. It follows, therefore, that the water test for 6 hours offers the best substitute for gin on this basis. This strengthens the evidence derived from the correlation coefficient, which points also to water-6 as the most promising substitute for gin.

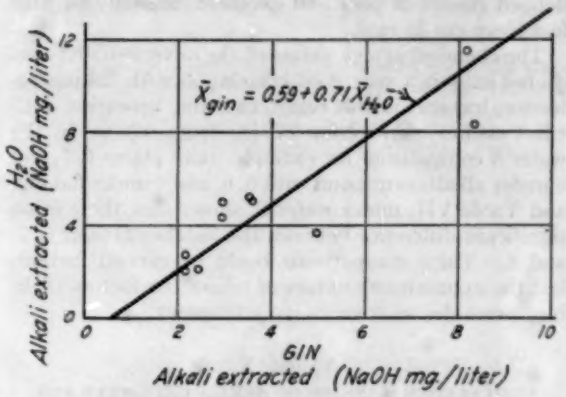

FIG. 4.—Correlation between gin and H_2O-8 with respect to alkali extracted.

The regression line in each of three cases fits the observed points better at the lower values of the extracted alkali (that is, better bottles in durability) than at the higher values. This would indicate that the correlation is higher in the region where the specification is to be defined.

(4) Correlation of Chemical Attack With Physical Behavior

The correlation of the analytically determined extracted alkali with the physical behavior of flaking is a more difficult task and yields less satisfactory results. The judging and estimation of the degree of flaking, unfortunately, are somewhat subjective. The bottles were examined carefully under a strong light by two observers who were not aware of the types of bottle at the time of inspection. The flaking was detected by reflected light from the flake surfaces, and the intensity of flaking was judged semiquantitatively by estimating the amount and size of the flakes present in the liquid. The bottles were ranked for flaking on this basis in each medium. These were compared with the ranks obtained from Table VI (using extracted alkali) by tabulation in Table IX.

The rank correlation coefficients, indicated as $\rho_{s,b}$ at the bottom of Table IX, were calculated by Spearman's rank correlation formula.[17]

Some relationship apparently exists between flaking and alkalinity for various media and also among the media, but its nature is obscure, and no reliable estimate can be made until a quantitative measure of flaking is available. Because flaking is measured sub-

[17] G. U. Yule and M. G. Kendall, *loc. cit.*, Chapter XIII.

jectively to a large extent in this study, the interpretation of the correlation coefficients that involve the "flake" ranking must be made with extreme caution.

It is to be noted that when a batch is definitely bad, for example, No. VI-a, there is no confusion concerning its behavior. A very good batch, for example, No. II-b, likewise exhibits characteristics which set it in a high rank on all counts. The other two batches, Nos. VII-a and II-a, which appear to lie respectively in the well-defined classes of poor and excellent, are only slightly less clean-cut in rank.

The chemical-attack values of the intermediate types do not exhibit a very good correlation with flaking behavior, but it is in this region that the "smearing-out" effect occurs as in section IV (2) (page 333). In the water-8 comparison, for example, rank places 6, 7, and 8 under alkali correspond with 6, 6, and 6 under flaking, and Table VII, under water-8, shows that there is no significant difference between the batches ranked 6, 7, and 8. These comparisons could be carried further, but the approximate nature of one of the factors (flaking) precludes such excessive refinement.

TABLE IX
COMPARATIVE RANKING OF ALKALI EXTRACTED AND FLAKING

	Gin		Alcohol		Water-6		Water-8	
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Batch	Alk.	Flak.	Alk.	Flak.	Alk.	Flak.	Alk.	Flak.
II-b	1	1	2	1	1	1	1	1
III-b	2	1	3	7	3	1	3	1
II-a	3	1	1	4	2	5	2	3
I-e	4	1	4	1	6	1	5	3
I-b	5	5	7	3	4	4	6	6
IV-a	6	8	5	10	8	7	8	6
V-a	7	7	6	8	7	7	7	6
I-f	8	5	9	6	5	7	4	9
VI-a	9	10	10	9	10	10	10	10
VII-a	10	9	8	4	9	6	9	5

$\rho_{1,2} = 0.82$ $\quad \rho_{2,1} = 0.73$
$\rho_{2,4} = 0.36$ $\quad \rho_{6,2} = 0.81$
$\rho_{2,6} = 0.68$ $\quad \rho_{7,2} = 0.86$
$\rho_{7,6} = 0.67$

The rank correlation coefficient for gin behavior ($\rho_{1,2}$) is relatively high and indicates that the alkali leached by the gin may serve as a measure of the flaking that occurs with gin. The other media exhibit lower correlation coefficients ($\rho_{2,4}$, $\rho_{6,6}$, and $\rho_{7,6}$), which indicates that co-variation of flaking and alkali extraction in these cases is not good. Additional data for these cases would be desirable.

Because the flaking of the gin medium is the ultimate behavior to be predicted, the alkali extracted by the other media was compared to the gin flaking ranks ($\rho_{2,2}$, $\rho_{6,2}$, and $\rho_{7,2}$). The water extraction apparently shows a rather high correlation with the flaking in gin.

A consideration of the various factors discussed (dispersion, rankings, and correlation) shows that, for the ten types of glass bottles examined, water exhibits characteristics which permit it to be substituted for gin in an accelerated test and which permit the interpretation of data in terms of flaking of gin with reasonable accuracy.

(5) Specifications

The alcohol data will not be considered in the following discussion because the low alcohol-gin correlation, as derived from this study, indicates that its use as a substitute medium for gin is probably limited.

In Table VIII (columns 1, 3, and 4), the original classification of the first three batch types into a top group is real. The difference between the highest average value in the top group and the lowest average value in the next intermediate group is 0.5 mg. per liter in the case of gin, 0.8 mg. per liter for water-6, and 0.9 mg. per liter for water-8. The average standard deviations in each case are respectively, 0.16, 0.14, and 0.14. These differences (0.5 to 1.0 mg. per liter), furthermore, can be readily detected by the titration technique that has been outlined and where it was shown that results could be duplicated to within 0.01 to 0.02 mg. of NaOH per liter.

The flaking behavior of these three top group batches is negative except for No. II-a for water-6.

An average value for a durability specification, based on the alkali extracted, apparently could be placed within the region of 2.7 to 3.2 mg. per liter for the three media to be used as a criterion for predicting, with reasonable accuracy, the probable flaking behavior.

Under previous considerations, however, the average value of the batch has been shown to be a necessary but insufficient condition to predict the behavior of the entire batch. The dispersion of the members of the batch, as measured by the standard deviation, is necessary to predict the percentage of bottles that may fall above a certain upper value (for example, 3.5 or 4.0 mg. per liter), beyond which the probability that flaking is high may be reasonably expected.

The remaining consideration in the problem of examining a practically "infinite" batch for a quality relating to a specification involves the size of the sample to be tested. The observed average value, $\bar{X}$, and standard deviation, σ, may differ from the true average, $\bar{X}'$, and the true deviation, σ'. This tendency of the observed values to vary from the true values is a result of sampling fluctuations and it is minimized as the sample size increases.

A sample size of 40 is a minimum below which estimations of the characteristics of the batch cannot be reliably made.

The assumption of a normal, or approximately normal, distribution of the quality of durability within any one batch underlies this entire treatment. The examination of this hypothesis can be accomplished with some degree of thoroughness only by the manufacturer of the container and not by the consumer.

V. Conclusions

(1) Alcoholic liquids may be tested for durability in an accelerated test at 90°C.

(2) A precision of $\bar{\sigma} = 0.01$ mg. of NaOH per liter has been attained in titrating alkali extracted by alcoholic and aqueous liquids.

(3) Judgment of results and prediction of batch characteristics are accomplished with greatest relia-

bility by use of the standard deviation function in addition to the average value.

(4) Simple integral ranking of quantitative data is shown to have limited value.

(5) The ten types of bottles examined are classified into three groups which exhibit the real differences between extracted alkali and flaking.

(6) A high correlation exists between the behavior of gin and water with respect to extracted alkali and flaking.

(7) A low correlation exists between the behavior of gin and alcohol with respect to extracted alkali and flaking.

(8) The order of magnitude of the alkali leached from the glass by gin during a 24-hour accelerated test at 90°C. is the same as that leached by water during a 6-hour accelerated test at 90°C.

(9) The correlation between extracted alkali and flaking is good for gin, fair for water, and poor for alcohol; the subjective nature of estimating flaking does not warrant a more precise comparison.

(10) A statistical analysis of the data indicates that a 6-hour accelerated test using water as a leaching medium may be substituted for a 24-hour test using gin, and the aqueous results may be used to predict, with some accuracy, the behavior of flaking in gin.

(11) The dispersion function and sample size, in addition to the average value, are important in setting up a specification.

Acknowledgment

The authors are grateful for the cooperation of the glass manufacturing companies in supplying bottles for the tests. They also wish to acknowledge the suggestions and assistance of L. Montant in the statistical analysis of the data and that of J. V. Peluso in the experimental portion of the work.

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PHOSPHATES IN CERAMIC WARE: III, PHOSPHORUS COMPOUNDS AS REDUCING AND FINING AGENTS IN GLASS*

By Woldemar A. Weyl and Norbert J. Kreidl†

Abstract

Phosphorus and phosphorus compounds, which are suitable fining and reducing agents for glasses to be melted under reducing conditions, have been applied in melting heat-absorbing and copper ruby glasses. Ferrophosphorus conveniently introduces both iron and a reducing agent for heat-absorbing glasses.

By balancing ferrophosphorus and red phosphorus or ferrophosphorus and sodium sulfate, it was possible to obtain glasses with the optimum FeO content under all melting conditions. The use of copper phosphide produced a superior copper ruby glass which strikes at a lower temperature and more rapidly.

I. Introduction

The appearance of gas bubbles or seeds in the finished glassware must be avoided. The evolution of gases in the glass melt is desirable only in the initial stage of the process because the rising bubbles contribute to homogeneity although these bubbles must be removed in the later stage of the melt. In normal soda-lime-silica glasses, the glass technologist has learned to improve the quality of the glass by the use of fining agents. Gehloff, Kalsing, and Thomas[1] have presented an explanation of the fining action which is generally accepted. According to these authors, a fining agent, such as arsenic, liberates oxygen in the melt, and the oxygen rises in the form of bubbles. As the partial pressure of H_2O and CO_2 is zero in the bubbles, these gases are removed from the melt; when the temperature is lowered, the excess oxygen can be reabsorbed by the glass.

Fining agents which liberate oxygen, however, cannot be used when the glass is melted under reducing conditions. Selenium ruby, copper ruby, carbon amber, and heat-absorbing glasses are typical examples of glasses melted under reducing conditions, and no satisfactory fining agent for this type of glass has yet been found.

To illustrate the action of fining agents, the problem of fining glass under oxidizing conditions will be analyzed first.

II. Glasses Melted Under Oxidizing Conditions

The nature of the gas bubbling through the melt is, theoretically, of no influence so long as it does not contain carbon dioxide and water and can be reabsorbed in a reversible reaction. All other gases will exert a sucking action on the adjoining glass phase and withdraw the gases from the melt.

* Presented at the Forty-Third Annual Meeting, The American Ceramic Society, Baltimore, Md., April 1, 1941 (Glass Division). Received March 12, 1941. For Parts I and II of this series, see W. A. Weyl, "I, In Opal Glasses," *Jour. Amer. Ceram. Soc.*, **24** [7] 221–25 (1941); "II, Role of Phosphorus in Bone China," *ibid.*, [8] 245–47.

† Research Fellow of the Monsanto Chemical Company Fellowship, Pennsylvania State College.

[1] G. Gehlhoff, H. Kalsing, and M. Thomas, "Fining of Glass," *Glastech. Ber.*, **8** [1] 1–24 (1930); *Ceram. Abs.*, **9** [8] 625 (1930).

For practical purposes, however, only oxygen can be used. Other gases would withdraw oxygen with the carbon dioxide from the melt and would thus impair the color. The withdrawal of oxygen would shift the iron oxide equilibrium toward FeO, the color of which is undesirable. The problem of decolorizing is therefore closely related to that of fining.

The ideal fining agent should meet the following requirements: (1) When it is added to the glass batch, the fining agent should preserve its gas content up to the fining range for otherwise it will not be effective; (2) the gas liberated in the fining range should be oxygen or at least a mixture rich in oxygen, otherwise, it will reduce the ferric iron; (3) the reaction responsible for the evolution of gas should be reversible, otherwise the last bubbles formed cannot be reabsorbed on cooling; and (4) the fining agent, or its reaction products, should not give rise to color either directly or when the glass is exposed to sunlight.

Kühl, Rudow, and Weyl[2] studied the behavior of different oxygen-producing agents, and their results are summarized in Fig. 1. The action of the various batch additions is represented by the amount of oxygen available with the progress of the melt.

(1) Effect of Fining Agents (Fig. 1)

Sodium sulfate acts as a fining agent; the reaction is reversible, inasmuch as gas bubbles that contain both sulfur dioxide and oxygen are readily absorbed when the temperature of the melt is lowered toward the working range. Only in the presence of reducing agents, such as carbon, does the fining effect disappear, and because the carbon reacts with the oxygen, the residual SO_2 can no longer be absorbed.

Arsenic and antimony behave in a similar way; they have to be oxidized to As_2O_5 and Sb_2O_5, respectively, and for that reason they are used together with saltpeter; the pentavalent oxides decompose gradually in the fining range, and this reaction is strictly reversible in the melt.

The action of cerium oxide as a fining agent is analogous to arsenic and antimony.

Saltpeter and potassium chlorate may not be used as fining agents because they decompose at too low a temperature; even if a nitrate or chlorate were known to decompose in the fining range, it would not be satisfactory because this reaction is not reversible.

Manganese compounds are excellent fining agents, although their color unfortunately prohibits general use, except for the purple manganese glasses and for other colored glasses where the presence of manganese is permissible.

Lead oxide in heavy lead glasses aids fining by its reaction with oxygen and alkali at low temperature and by the decomposition of the plumbates formed at high temperature.

[2] C. Kühl, H. Rudow, and W. Weyl, "Behavior of Oxygen-Releasing Compounds in Glass in the Melting and Fining Process," *Glastech. Ber.*, **16** [2] 37–51 (1938); *Ceram. Abs.*, **17** [6] 214 (1938).

III. Glasses to Be Melted Under Reducing Conditions

For glasses that must be melted under reducing conditions, no corresponding fining agents are available.

In the case of the selenium ruby glass, this is not very serious because the melt is supersaturated with cadmium sulfide and selenium, both of which have such a high vapor pressure that they boil out of the melt. Their volatility, of course, is undesirable, but it helps to free the glass of bubbles.

The carbon amber glasses offer serious difficulties in fining, and many attempts have been made to find a suitable fining agent. Alkali chlorides and calcium fluoride are used but with doubtful success.

The same difficulties arise in the manufacture of copper ruby and heat-absorbing glasses.

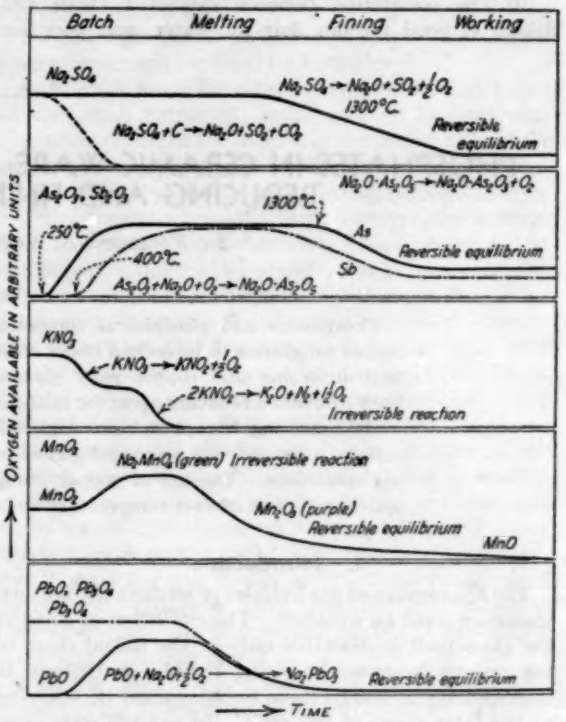

FIG. 1.—Behavior of different oxygen-producing agents.

In the present studies on the use of phosphates in ceramics and phosphorus compounds in general, red phosphorus and metal phosphides were found to be successful both as fining agents and as reducing agents. In a patent relating to the manufacture of colorless heat-absorbing borate and phosphate glasses, Berger[3] pointed out the advantage of ferrophosphorus and other phosphorus compounds as reducing agents.

IV. Heat-Absorbing Glasses

The infrared absorption of the ferrous iron in aqueous solutions and glasses has been used for the production

[3] E. Berger, "Heat-Absorbing Glass," U. S. Pat. 1,961,603, June 5, 1934; *Ceram. Abs.*, **13** [8] 207 (1934).

of heat screens. Because only the ferrous iron (not ferric iron) possesses this property, the oxidation equilibrium between the two oxides must be shifted as far as possible toward FeO. Only under these circumstances can heat-absorbing glasses of maximum efficiency with a minimum loss of visible light be obtained. Silicate glasses that contain all of the iron in the lower state of valency do not exist. According to Bowen and Schairer,[4] FeO in silicate melts decomposes partly into Fe_2O_3 and metallic iron. Before these important studies on phase equilibria were made, it had been difficult to understand why continued reduction did not lead to colorless glasses when all of the iron was present in the bivalent state.

Iron is usually added to the glass batch as ferric oxide, which is reduced in the melt by the addition of carbonaceous material. For more expensive glasses, such as goggles, ferrous oxalate has been used successfully, but its high price prohibits its general application.

To study the possible use of ferrophosphorus in the production of heat-absorbing glasses, a series of experiments was carried out. A normal soda-lime-silicate glass was used as a base.

The iron content of the ferrophosphorus* used corresponds to 95.7% of FeO or 106.3% of Fe_2O_3. The melts were carried out in kyanite crucibles in an electrical furnace, that is, under oxidizing conditions. The amount of glass melted varied from 100 to 250 gm. Compared with plant conditions, the atmosphere and the surface-volume ratio were unfavorable for the reduction of the iron, but good results were obtained with ferrophosphorus.

When less than 1% of ferrophosphorus was introduced, the reducing power proved to be insufficient under the conditions of the present study, and greenish glasses resulted. With about 2% of ferrophosphorus, pure blue colors were obtained, indicating the presence of an optimum amount of FeO. The addition of more than 2% of ferrophosphorus gave rise to brown colors, indicating the presence of an excess of iron phosphide in the glass. These percentage figures, however, have no absolute value as they change with melting conditions and with melting time.

In all cases where only a small amount of iron was desirable, the amounts of ferrophosphorus required did not offer sufficient reduction. The addition of red phosphorus proved to be advantageous both for the reduction of the iron and for the fining of the melt. If, on the contrary, the reducing conditions were strong enough to keep iron phosphide in solution, the proper degree of oxidation was accomplished by adding small amounts of sodium sulfate to the batch.

By balancing ferrophosphorus and red phosphorus or ferrophosphorus and sodium sulfate, it was possible to obtain glasses with the optimum FeO content under all melting conditions.

V. Copper Ruby Glass

The results obtained with ferrophosphorus as a reducing agent in heat-absorbing glasses stimulated analogous experiments with copper ruby glasses. The color of copper ruby is caused by metallic copper in a finely divided colloidal state. Copper ruby glasses are produced by melting copper glasses that contain tin oxide under reducing conditions. Cuprous ions are formed, which on cooling and reheating decompose into cupric ions and metallic copper as follows:

$$Cu_2O \rightarrow CuO + Cu \qquad (1)$$

This reaction shows that even under ideal conditions only one half of the copper changes into the metallic state. Under practical conditions, however, the reduction in the melt cannot be carried far enough to change all of the copper present into the cuprous state. More cupric oxide than metallic copper is therefore to be expected in the finished ware. Because the copper ions give rise to a green color, copper ruby contains the particles of metallic copper in a greenish matrix. This fact is responsible for the dark and dull shades of the copper ruby as compared with the brilliant shades obtained from gold ruby.

In the present study, efforts have been made to improve the ruby color by eliminating reaction (1) and by substituting another reaction which does not lead to cupric oxide. One reaction meeting this requirement is known in metallurgical operations where cuprous oxide reacts with copper sulfide to form metallic copper (reaction (2)).

$$2\,Cu_2O - Cu_2S \rightarrow 6\,Cu + SO_2 \qquad (2)$$

That this reaction is possible, even within the glass melt, may be deduced from the observations of Zsigmondy,[5] who included copper sulfide in his experiments on the solubility of metal sulfides in glass but was surprised to obtain copper ruby in some cases.

The use of copper sulfide for this purpose is limited by its extremely low solubility in the glass.

Copper phosphides seem to be more soluble. The use of red phosphorus in the production of copper ruby glass is therefore more advantageous. A reaction, similar to reaction (2), seems to take place, which leads to metallic copper and phosphoric acid, reaction (3).

$$5\,Cu_2O + 2\,CuP \rightarrow 12\,Cu + P_2O_5 \qquad (3)$$

The writers did not try to determine whether the formation of metallic copper was caused by copper phosphide, elemental phosphorus, or hypophosphite inasmuch as the mechanism of the reaction has little bearing on its application. Several phosphorus compounds are known which precipitate metallic copper from aqueous solutions of copper salts.

The superiority of producing copper ruby, according to reactions (2) or (3) over the type of reaction (1)

[4] (*a*) N. L. Bowen and J. F. Schairer, "System FeO–SiO_2," *Amer. Jour. Sci.*, **24** [5] 177–213 (1932); *Ceram. Abs.*, **12** [2] 83 (1933).
(*b*) N. L. Bowen, J. F. Schairer, and E. Posnjak, "System CaO–FeO–SiO_2," *Amer. Jour. Sci.*, **26**, 193–284 (1933).

* The ferrophosphorus used was obtained from the Monsanto Chemical Company; this Company also kindly furnished the following analysis: Fe 74.37, P 25.48, and Si 0.15%.

[5] R. Zsigmondy, "Solubility of Sulfides in Glass," *Dinglers Polytech. Jour.*, **273**, 29–37 (1889).

might explain why the introduction of copper as a cyanide represents an improvement. This method, which was suggested by Dobrovolny,[6] has found practical application.

The observations of the writers on the fining and reducing of copper glasses were in full agreement with what was expected from the previous experiments on heat-absorbing glasses. There also seems to be a particular influence of phosphorus compounds on the development of the copper ruby color. The copper ruby glass strikes at lower temperatures and more rapidly.

In many old formulas of copper ruby glasses, phosphates had been added in the form of bone ash, and it seems possible that the formation of phosphates in the glasses is responsible for the ease of striking. Gold ruby glasses with phosphate additions were therefore studied to decide whether the phosphates have a direct bearing on the ease of striking. These glasses are not sensitive to reducing or oxidizing influences, and the action of phosphorus on gold ruby, consequently, cannot be traced back to its reducing power. Indeed, the writers found that the addition of alkali phosphates up to 3% also had a beneficial effect on the striking of gold ruby, for which result the following explanation is suggested. The introduction of bone ash or alkali phosphates into soda-lime or potash-lead-silica glasses leads to the formation of apatite crystals. This has been pointed out in the first paper of this series.* It might be possible that nuclei of these crystals have a decisive influence on the precipitation of the metal phase and therefore on the ease of striking of gold and copper ruby.

In this specific case, the formation of phosphates, as a result of the oxidation of the phosphorus compounds, must have been responsible for this phenomenon.

VI. Conclusions

In presenting these observations on the behavior of phosphorus compounds as fining and reducing agents, the writers hope to stimulate interest in further research and in large-scale experiments. The results obtained are applicable to carbon amber glass as well as to other glasses where reducing conditions are desirable throughout the melt. The glasses studied, specifically heat-absorbing glasses and copper ruby, are not suitable for small-scale experiments. The results, however, indicate that further studies are promising.

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[6] F. J. Dobrovolny, J. M. Youel, and H. E. Klein, "Colored Glass," U. S. Pat. 2,174,554, Oct. 3, 1939; *Ceram. Abs.*, **19** [1] 11 (1940).

* See star (*) footnote, p. 339.

CERAMIC ABSTRACTS

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Ross C. Purdy, Editor

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Journal Reference: The journal name appears in italics, followed by the volume (bold-faced), issue number (in brackets), page numbers, and year (in parentheses).

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Abrasives

Abrasive paper and cloth. P. A. Benord. *Melliand Textilber.*, **22**, 91–96 (1941); *Chem. Abs.*, **35**, 4929 (1941).—Manufacturing methods are described.

Grinding for the preparation of metallographic specimens. T. Berglund. *Jernkontorets Ann.*, **124** [6] 234–64 (1940).—B. made a thorough investigation of the factors influencing the grinding and polishing of metallographic specimens. The specimens used were of chromium-nickel steel, 15 to 30 mm. in diameter, hardened to Brinell 265. Three types of polishing disks were used: (*a*) aluminum disks to which Alundum polishing cloths were attached, (*b*) lead disks with a spiral groove to which a medium of emery powder in lard oil was applied, and (*c*) molded disks made of Alundum 2600 gm., paraffin 240 gm., and stearine 160 gm. R.A.R.

Industry's $100,000,000 tool. Walter Holbrook. *Popular Science Monthly*, **139** [1] 98–102 (1941).—Abrasives are the key to the machine age. Since the start of World War II, the personnel of the abrasive industry has been doubled to 20,000 men making 100,000 kinds of grinding wheels. Improved grinding wheels have reduced tolerances to $^1/_{25,000}$ of an inch. The production and use of diamond, silicon carbide, aluminum oxide, and boron carbide wheels are described. A diagram shows the flow of bauxite, clay, and feldspar into a grinding wheel in use. A.P.

Surface layer of silicon carbide and the conversion of silicon carbide into cristobalite. H.-G. Heine and P. Scherrer. *Helv. Phys. Acta*, **13**, 489–97 (1940); *Chem. Abs.*, **35**, 4652 (1941).—X rays and 30-kv. electrons showed no evidence of a surface layer on untreated SiC crystals; the existence of such a layer is indicated by electrometric measurements. It is concluded that the layer must be less than 10^{-7} cm. thick. A thicker layer was prepared by heating a crystal of SiC at 1300° for 5 to 7 hr. in the presence of air. X-ray examination of such a crystal showed nothing but the SiC structure, but electron diffraction indicated a surface layer of cristobalite. At 1500° the crystal was completely changed to cristobalite in 2 to 3 hr. Siloxicon is a mixture of SiC, a little graphitic C, and SiO_2 in the form of cristobalite.

PATENTS

Abrading machine. C. J. Astrowski and F. J. Fritz (General Electric Co.). U. S. 2,251,607, Aug. 5, 1941 (June 28, 1939).

Abrasive article and method of manufacture. Fred Brown (Carborundum Co.). U. S. 2,251,437, Aug. 5, 1941 (Nov. 15, 1937).

Apparatus for holding and grinding flexible blades. A. A. Kottmann. U. S. 2,252,892, Aug. 19, 1941 (Feb. 28, 1939).

Buffing wheel. C. J. Peterson and A. H. Peterson. U. S. 2,251,690, Aug. 5, 1941 (June 11, 1940).

Cam-grinding machine. C. J. Green (Norton Co.). U. S. 2,251,882, Aug. 5, 1941 (May 17, 1940).

Centerless grinders. A. Scrivener, Ltd., and A. Scrivener. Brit. 537,641, July 9, 1941 (April 8, 1940).

Coated abrasive. N. E. Oglesby (Behr-Manning Corp.). Can. 397,579, July 1, 1941 (Oct. 16, 1937; in U. S. Feb. 6, 1937). G.M.H.

Compound applicator for buffing machines. C. I. Packer and E. H. Kammerer (Packer Machine Co.). U. S. 2,251,161, July 29, 1941 (March 2, 1940).

Cylindrical grinding and lapping machine. Norton Co. Brit. 537,633, July 9, 1941 (March 9, 1939).

Device for feeding rods or tubes in grinding machines, etc. Aktiebolaget Malcus Holmquist. Brit. 537,022, June 18, 1941 (March 4, 1939).

Device for lapping tap chasers. H. M. Johnston (National Tube Co.). U. S. 2,250,380, July 22, 1941 (Oct. 19, 1939).

Drill grinder. E. C. Oliver. U. S. 2,252,303, Aug. 12, 1941 (March 7, 1939).

Dustless grinder. R. W. Bishel. U. S. 2,252,455, Aug. 12, 1931 (April 22, 1939).

Granular coated material. R. L. MELTON, R. C. BENNER, AND H. P. KIRCHNER (Carborundum Co.). Can. 398,270, July 29, 1941 (April 29, 1940). J. A. WILLIAMSON (Carborundum Co.). Can. 398,271, July 29, 1941 (April 29, 1940). G.M.H.

Granular coated web manufacture. R. L. MELTON, R. C. BENNER, AND H. P. KIRCHNER (Carborundum Co.). Can. 398,269, July 29, 1941 (April 29, 1940). G.M.H.

Grinding machine. R. H. CRAMER (General Motors Corp.). U. S. 2,253,324, Aug. 19, 1941 (Sept. 24, 1937). H. E. SOMES AND F. J. MUELLER. U. S. 2,252,818, Aug. 19, 1941 (July 31, 1940).

Grinding-machine footstock. H. S. INDGE (Norton Co.). U. S. 2,251,885, Aug. 5, 1941 (April 25, 1941).

Grinding wheel. M. J. GREGORY (Caterpillar Tractor Co.). U. S. 2,250,580, July 29, 1941 (Dec. 26, 1939).

Grinding wheel truing apparatus. C. C. ALVORD (Norton Co.). Can. 398,316, July 29, 1941 (July 24, 1939). W. H. WOOD (Norton Co.). Can. 397,825, July 8, 1941 (April 27, 1939; in U. S. May 4, 1938). G.M.H.

Lapping machine. L. R. BROWN (Monroe Calculating Machine Co.). U. S. 2,251,033, July 29, 1941 (Feb. 23, 1940).

Lapping machine for finishing metal surfaces. NORTON CO. Brit. 537,632, July 9, 1941 (Feb. 28, 1939).

Machine for finishing the surface of a cylindrical workpiece by abrasion. CINCINNATI GRINDERS, INC. Brit. 537,246, June 25, 1941 (April 10, 1939).

Machine for grinding cylindrical surfaces. W. H. HARRIS, JR. (Micromatic Hone Corp.). U. S. 2,252,176, Aug. 12, 1941 (Dec. 19, 1936; renewed Nov. 15, 1939).

Manufacture of abrasive-coated webs. J. A. WILLIAMSON (Carborundum Co.). U. S. 2,250,119, July 22, 1941 (March 25, 1940).

Manufacture of granular-coated products. F. J. TONE AND H. C. MARTIN (Carborundum Co.). U. S. 2,252,587, Aug. 12, 1941 (Oct. 12, 1933; May 13, 1936).

Method of form setting abrasive disks. F. O. ALBERTSON (Albertson & Co., Inc.). U. S. 2,252,683, Aug. 19, 1941 (April 29, 1939).

Mounting for abrading wheels. JAMES ENGLISH. U. S. 2,251,702, Aug. 5, 1941 (May 16, 1940).

Portable disk-abrading machine. A. N. EMMONS (Porter-Cable Machine Co., Inc.). U. S. 2,251,442, Aug. 5, 1941 (July 24, 1937).

Production blade grinder. G. J. CALAME. U. S. 2,252,879, Aug. 19, 1941 (Feb. 15, 1939).

Saw-sharpening apparatus. E. J. BUCKNAM. U. S. 2,249,743, July 22, 1941 (Oct. 13, 1939).

Tapered honing tool. J. E. KLINE (Micromatic Hone Corp.). U. S. 2,252,809, Aug. 19, 1941 (Feb. 18, 1939).

Waterproof abrasive block. LLOYD A. HATCH (Minnesota Mining & Mfg. Co.). Can. 397,822, July 8, 1941 (May 1, 1939). LLOYD A. HATCH AND GEORGE NETHERLY. Can. 397,716, July 8, 1941 (Jan. 30, 1936). G.M.H.

Way grinding machine. CHRISTIAN BALDENHOFER (Thompson Grinder Co.). U. S. 2,252,877, Aug. 19, 1941 (Oct. 13, 1939).

Art and Archeology

Athenian astragalos. G. M. A. RICHTER. *Bull. Metropolitan Mus. Art*, **36** [5] 122–23 (1941).—Greek potters of the classical period concentrated on wheel-made vases, the technique of molding being reserved for small vases in the form of heads or objects known as terra-cotta sculptures. The Museum has acquired a rare example of this class, a magnified knucklebone or *astragalos* (illustrated). These large terra-cotta shapes may have been used as containers for real knucklebones, which were used by Greek children for a game similar to jackstones. The artist painted the two long sides, leaving the others covered only with a thin black glaze. The style suggests that it was painted about 460 B.C. by a contemporary of the Sotades Painter, perhaps an associate of the Penthesilea Painter; it depicts the flying Eros playing the lyre and enclosed palmettes and scrolls. Like the other two or three known examples, this one was pressed in a two-piece mold. Although made at the same time, the molds are all different, showing that there was competition among Athenian potters. Each was probably made in a different pottery. A.A.A.

Banded glass bowl of the 1st century A.D. C. A. *Bull. Metropolitan Mus. Art*, **36** [1, Sect. 1] 21 (1941).—The banded glass bowl recently acquired by the Museum is a rare variation of millefiori glass, an invention of Ptolemaic Egypt. The bowl belongs to the 1st century A.D. and was exported to Russia from Alexandria. Since it first appeared before the public in 1908 at an auction of Hellenistic antiquities at Nikolaev, Russia, it has belonged to three great collections. It is divided by a cross made of an opaque yellow square alternating with millefiori sections in a purple and white pattern. The sections between the arms of the cross are filled with chevrons in translucent colors (white, purple, blue, and yellow). The lip of the bowl is finished off with a purple rod wrapped with a white spiral. This bowl owes its quality to its fine color and to its intricate though seemingly simple pattern. A.A.A.

Characteristic nature of the glaze of some famous earthenware and porcelains in Kyushu, Japan. EITI KOIZUMI. *Jour. Chem. Soc. Japan*, **62**, 194–98, 288–90 (1941); *Chem. Abs.*, **35**, 4929 (1941).—The ashes of plants used as the glaze are analyzed, and the results are summarized. The results of chemical analyses of various glazes are given. See *Ceram. Abs.*, **20** [4] 97 (1941).

Discussion on "Symbolism in Chinese porcelain decoration." LAWRENCE E. BARRINGER. *Bull. Amer. Ceram. Soc.*, **20** [8] 287–88 (1941).—2 references. See *ibid.*, [6] 196–207.

German and Austrian porcelains. C. LOUISE AVERY. *Bull. Metropolitan Mus. Art*, **36** [4] 97–98 (1941).—A small group of German porcelain figures made at Höchst about 1750 to 1760 includes a statuette of a gardener made at Fulda (illustrated) and one of Marie Antoinette. There is also a coffeepot of Höchst porcelain painted by an independent decorator, Gerverot, who copied a garden scene from a print by the Augsburg engraver Johannes Esaias Nilson, whose interpretations of the rococo style strongly influenced German porcelain development. The Museum has also acquired a rare piece of Vienna porcelain, a small bust of Francis I, husband of Maria Theresa. This is presumed to have been made by Johann Josef Niedermayer, who was in charge of figure modeling at the Vienna Factory from 1747 to 1784. A.A.A.

Gift of Islamic pottery. M. S. DIMAND. *Bull. Metropolitan Mus. Art*, **36** [3] 70–73 (1941).—A recent gift of Mohammedan ceramic art from Horace Havemeyer comprises fourteen Persian tile of the 13th and 14th centuries, a Turkish tile of the 16th century, and an early 17th-century Turkish flower vase. A Persian wall tile with luster decoration, a Persian corner tile with luster decoration (second half of the 13th century), and a Persian wall tile with overglaze decoration (beginning of the 14th century) are illustrated. A.A.A.

Gift of Italian majolica. C. L. A. *Bull. Metropolitan Mus. Art*, **36** [6] 141–42 (1941).—A 15th-century spherical majolica vase from Faenza recently presented by Mr. and Mrs. George Blumenthal has an all-over design of peacock feathers interrupted by two circular medallions enclosing the sacred monograms combined with a cross, symbolizing the immortality and infinity of Christ. A.A.A.

Great sculpture of the Italian Renaissance in the National Gallery. ALFRED M. FRANKFURTER. *Art News*, **40** [9] 8–12 (1941).—In discussing the rediscovery of the three-dimensional classic by the sculptors of Italy from 1300 to 1600, F. uses as examples some excellent illustra-

tions of terra-cotta pieces by Donatello, Vittoria, Pollaiuolo, Verrocchio, and the famous Della Robbias. M.E.P.

Modern American ceramics and enamel. C. L. A. *Bull. Metropolitan Mus. Art*, **36** [3] 77–78 (1941).—From the Ninth National Ceramic Exhibition sponsored by the Syracuse Museum of Fine Arts (*Bull. Amer. Ceram. Soc.*, **19** [11] 453–55 (1940)), the Metropolitan Museum has purchased a large stoneware bowl with slip decoration made by Marion L. Fosdick, a vase by Maija Grotell (a potter of Finnish birth now teaching in the Cranbrook Academy of Art, Bloomfield Hills, Mich.), and an enameled plate by Karl Drerup. A.A.A.

Passion window in East Brent Church, Somerset. Christopher Woodford. *Jour. Brit. Soc. Master Glass Painters*, **8**, 96–100 (1941).—The window has three lights and shows nine scenes. The glass is almost wholly of the 19th century. It is in the style of the 15th century, but is so cleverly executed that it might be mistaken for a window of ancient glass. It was probably manufactured in Bristol or Gloucester so that the glass could be readily transported by water to its destination. Illustrated. 5 references. M.B.H.

Prehistoric, aboriginal pottery of the Peoria, Ill., region. Ethel Schoenbeck. *Trans. Illinois State Acad. Science*, **33** [2] 44 (1940).—S. describes the types of pottery characteristic of the various cultural developments of this area as represented by ware collected by the Archeological Section of the Peoria Academy of Science. B.C.R.

Recent purchases of Early American glass. Marshall Davidson. *Bull. Metropolitan Mus. Art*, **36** [5] 124–25 (1941).—Four outstanding examples of post-Revolutionary glass, with no counterparts in the Museum's collections, have recently been acquired. The most impressive is a large covered bowl in an unusual shade of blue, suggesting the influence of southern New Jersey glass blowing. A green bottle-glass ewer seems traceable to Connecticut. The two other pieces may be ascribed to a glasshouse operating during the first part of the 19th century in the Pittsburgh-Ohio district. A pitcher in yellow-green glass is typical of that region. A graceful amber compote, a rarity in American glass of that period, was probably made in Zanesville, Ohio. Illustrated. A.A.A.

Roman glass jug. C. A. *Bull. Metropolitan Mus. Art*, **36** [6] 142 (1941).—A glass jug of the Roman imperial period, from the estate of Madeleine F. Astor Dick, has an attractive shape, with a flaring lip and offset foot. The clear greenish glass has developed a beautiful iridescence from weathering. A.A.A.

Three Chinese vases. A. P. *Bull. Metropolitan Mus. Art*, **35** [12] 261–62 (1940).—Two T'zu-chou vases and one unfinished blue and white vase have recently been acquired for study purposes. The T'zu-chou vases illustrate the technique used in the magnificent T'zu-chou ware of the Sung dynasty. Both are of reddish stoneware covered with a white kaolin slip; one has a cloud design painted on the slip, and the other has an incised floral decoration. Both are unglazed. The third piece is bottle-shaped. It is of fine white porcelain painted with a design of cobalt. If it had been glazed it would have become one of the brilliant blue and whites of the K'ang Hsi period. A.A.A.

Three gifts of English ceramics. C. Louise Avery. *Bull. Metropolitan Mus. Art*, **36** [3] 65–67 (1941).—Eight pieces of English ceramics given by R. T. Wilson illustrate the modeling and the beautiful mottled glazes associated with the name of Thomas Whieldon. Three Whieldon-type vases, four Ralph Wood figures, and a well-known portrait bust by Enoch Wood were presented by Mrs. Frances P. Garvan. The most important of the group by Ralph Wood is the equestrian figure of the Duke of Cumberland arrayed as a Roman emperor. It is of fine light-colored clay in harmonious colors and has a glaze of liquid quality. The portrait bust of the great Methodist preacher, George Whitefield, is one of the finest examples of the work of Enoch Wood. These pieces show important trends in English pottery of the second half of the 18th century, e.g., the use of simple themes, the adaptation of Oriental models, the revival of classic styles, and the commemoration of events or people. The Chelsea porcelain vase recently presented by Mr. and Mrs. Howard Eric shows the same tendencies in a more sophisticated manner. A.A.A.

Venetian enameled glass goblet. *Art News*, **40** [10] 16 (1941).—A full page color print with overleaf description shows a goblet from the workshop of the Berovieri (ca. 1475). Angelo Beroviero and his sons derived their technique from the Saracenic glassmakers of the Levant, and at their Murano shop Angelo was known as the inventor of the lavish type of enamel decoration shown on this goblet. It is likely, however, that he learned the Eastern art of mixing metallic oxides for these enamels from his friend, the alchemist Paolo da Pergola. This goblet, the broken foot of which has been replaced by velvet-covered wood, is now in the Toledo Museum of Art after having come to this country from England by British Navy convoy. M.E.P.

World's Fair P. S.: Mural for Cleveland station. Anon. *Art News*, **40** [8] 33 (1941).—The porcelain enamel-on-steel mural which decorated the Home Furnishings Building has been placed in the Union Terminal Station in Cleveland, where the original symbolism of the design (man's struggle against the elements, represented by a series of furiously riding figures) is equally well suited to represent phases of travel. M.E.P.

PATENTS

Ceramic pigment. C. J. Harbert (Harshaw Chemical Co.). U. S. 2,251,829, Aug. 5, 1941 (July 25, 1939).—Yellow to brown ceramic pigments consist essentially of the oxides of chromium, tungsten, and titanium in the form of a calcination product in approximately the following proportions: Cr_2O_3 (1 mol.) and WO_3 (1 to 3 mol.) 5 to 15 parts by weight and TiO_2 95 to 85 parts by weight.

Designs for:

Bottle. A. I. Lorenzen (Owens-Illinois Glass Co.). U. S. 128,668, Aug. 5, 1941 (Dec. 14, 1940).

Jar. E. J. Walker and R. B. Stover (Owens-Illinois Glass Co.). U. S. 128,650, Aug. 5, 1941 (June 6, 1941).

Plate. Isobel Darrow (Pacific Clay Products). U. S. 128,662 to 128,665, Aug. 5, 1941 (May 26, 1941).

Cements

Developments and trends in the manufacture of cement, lime, and gypsum. Nathan C. Rockwood. *Rock Products*, **44** [1] 72 (1941).—R. reviews the developments in the manufacture of these products during 1940. B.C.R.

Influence of the heat treatment of Portland-cement clinker on the properties of the cement. T. W. Parker. *Jour. Soc. Chem. Ind.* [London], **58** [6] 203–13 (1939).—P. studied the effect of the manner in which Portland cement is cooled from the clinkering temperature on the properties of the resultant cement. Two general types of clinker were examined, viz., those in which rapid cooling resulted in a portion of the clinker being converted into glass and those in which annealing produced a product approaching full chemical equilibrium. The cements obtained by grinding these clinkers were tested by small-scale methods to determine setting time, soundness, strength, resistance to chemical attack by sulfate solutions, shrinkage, and heat of hydration. For the range of compositions tested, the main difference between the types was the considerably increased resistance to sulfate attack of the "glassy" type. The setting time of the "glassy" cements was easier to control than that of the annealed cements, and the strength at 28 days and the heat of hydration were higher. The

annealed clinker required less time for grinding to a given fineness than the "glassy" clinker. G.R.S.

Rapid method of determining alkalis in cement. FRANCIS W. GLAZE. *Rock Products*, **44** [7] 42 (1941).—There is a growing belief that alkalis affect the properties of Portland cement considerably, largely because of the formation of complex molecules. California has established a limit of 0.5% on the amount of alkali that may be present in Portland cement used for highway construction; consequently, there is need for a rapid method of determining alkalis. The following method provides for an accurate and rapid determination of Na_2O and K_2O. Treat 1 gm. of cement with water and HNO_3 until it is completely disintegrated. Fume with $HClO_4$ and HF until the excess $HClO_4$ is driven off. Ignite gently (not over 500°C.), digest with water, filter, and wash with water. Acidify the filtrate and washings, amounting to about 125 ml., with HCl and evaporate, finally making up to 100 ml. Determine Na_2O in an aliquot portion (10 ml.) using the uranyl zinc acetate method. Precipitate the potassium as potassium chloroplatinate. Transfer the washed precipitate of potassium chloroplatinate to a 250-ml. beaker and dilute to 100 ml., slightly acidify with HCl, immerse a piece of magnesium ribbon (0.5 gm.), and digest on a steam bath. When the action ceases or the solution becomes cloudy due to the formation of basic magnesium salts, add 2 ml. HCl, boil, filter, and wash with hot water. The paper and precipitated platinum are ignited and weighed. Na_2O and K_2O can be determined in a 7-hr. day as compared with 3 days for the A.S.T.M. method. B.C.R.

Enamel

Combination powder and wet process enameling for cast iron. ANON. *Sprechsaal*, **73**, 147–48 (1940); abstracted in *Chem. Zentr.*, **1940, I**, 3973.—The advantages of the powder enameling and wet enameling processes can be obtained without their disadvantages by means of a special mica ground. This ground is a very hard melt ground for cast iron to which a large quantity of mica can be added by grinding. Potash mica is best suited for this purpose. M.V.C.

Making the most of porcelain enamels. ANON. *Elec. Mfg.*, May (1941); reprinted in *Better Enameling*, **12** [5] 10–12, 24, 26 (1941).—The possibilities of developing uses for porcelain enamel on new products are discussed. White enamels have been developed that require a thickness of only 0.006 in. (over ground coat) to provide greater resistance to damage by impact. Factors governing design, care of enamels, and proper type of sheet iron to be used are also discussed. 10 illustrations. B.C.R.

Meeting production demands through proper planning. DANA CHASE AND ED GOETZ. *Better Enameling*, **12** [4] 4–8, 22–24 (1941).—The equipment, control setup, and production planning of the Geo. D. Roper Corp. enameling plant are discussed. 25 illustrations. B.C.R.

Metal & Thermit Corp. builds new research laboratory. ANON. *Bull. Amer. Ceram. Soc.*, **20** [8] 296 (1941).

Molybdenum in enamels. A. DIETZEL. *Emailwaren-Ind.*, **18** [13–14] 30–31 (1941).—In 1912 the Vereinigte Chemische Fabriken, Vienna, Austria, obtained a patent (65,037) on the use of molybdenum compounds (and tungsten) to make enamels adherent. These compounds have an action similar to that of cobalt and nickel oxides with the added advantage that they do not color the enamel. If the e.m.f. between molybdenum and iron is measured at 900° in an electrolyte such as borax, the values obtained are about 0.2 and 0.3 volt, varying according to the MoO_3 and FeO concentrations in the melt. Molybdenum is as noble as Ni toward iron, which explains the adherence of molybdenum compounds in ground enamels. The photomicrograph of enameled cross sections fired with about 5% MoO_3 is similar to that of nickel or cobalt enamels; countless particles of metallic molybdenum can be seen, indicating that the secondary reaction $MoO_3 + 6FeO = Mo + 3Fe_2O_3$ occurs. For adherence, only the reaction $3Fe + MoO_3 = 3FeO + Mo$ is necessary; the Mo then forms the local element with Fe which corrodes the surface of the iron. Besides affording a lighter ground, molybdenum in combination with antimony opacification permits the development of a white ground. Tungsten shows no such adherence. M.V.C.

Relation between nickel deposit and adherence. J. M. ZANDER. *Better Enameling*, **11** [12] 10–13 (1940).—The use of a nickel dip in preparing enameling-iron surfaces is good insurance against many defects that are apt to occur, although consistent results are lacking. The effects of immersion time, pH, and the temperature of the bath on the nickel coating obtained were studied. A loss of adherence at firing temperatures between 1500° and 1580°F. occurred if the nickel deposit became too heavy; a rigid control of the factors governing the deposition of the nickel film is therefore essential. A minimum nickel deposit of 0.025 gm. per sq. ft. was necessary to obtain good adherence for a normal ground coat fired at 1560° to 1580°F. for 4 min. 6 charts. B.C.R.

Relation of the particle sizes of the frit and color oxides to the color properties of porcelain enamels. ANDREW I. ANDREWS AND RALPH L. COOK. *Jour. Amer. Ceram. Soc.*, **24** [9] 298–310 (1941).—10 references, 26 figures.

Sponge rubber helps correct one-coat ware defects. ANON. *Better Enameling*, **12** [3] 12 (1941).—The damage to the finish enamel of one-coat ware during brushing may be prevented by the use of a sponge-rubber top on brushing tables, turntables, and other equipment upon which the ware is placed during processing. B.C.R.

Three-hoist electric traveling crane facilitates pickling operations. W. J. ALBRECHT. *Ceram. Ind.*, **36** [4] 102 (1941).—A specially equipped electric crane for carrying refrigerator parts through the cleaning and pickling cycles is described briefly. The crane is installed at the General Electric Co. plant at Erie, Pa. Illustrated. H.T.

Use of porcelain enamel in the gas-fired furnace field. ANON. *Better Enameling*, **11** [11] 7–10, 28 (1940).—New and wider usage of porcelain enameled materials is discussed. 7 illustrations. B.C.R.

PATENTS

Porcelain enamel. M. J. BAHNSEN AND E. E. BRYANT (Ferro Enamel Corp.). U. S. 2,250,456, July 29, 1941 (Dec. 28, 1939).—A porcelain enamel frit of the character produced by smelting a raw batch mixture of the following composition: silica sand 2.85, dehydrated borax 18.15, feldspar 24.90, zircon sand 19.30, sodium nitrate 1.15, fluorspar 4.55, sodium fluosilicate 16.25, bone ash 5.30, aluminum hydrate 4.90, and zinc oxide 2.65%. **U. S. 2,250,457,** July 29, 1941 (Oct. 16, 1940).—A method of making a porcelain enamel article having an opaque coating comprises smelting an antimony-free raw batch mixture of fusible enamel ingredients to form a relatively fluid melt containing phosphorus in an amount equal to about 2 to 3% of P_2O_5 and zirconium oxide in an amount equal to about 11 to 14%, milling a slip containing the frit, coating the ware with the slip, and firing it to form the opaque surface.

Supporting structure for porcelain enameled pans. A. E. FELLNER (Porcelain Structures, Inc.). U. S. 2,251,991, Aug. 12, 1941 (Jan. 25, 1940).

Vitreous enamel opacifier. R. J. WHITESELL (Röhm & Haas Co.). U. S. 2,252,588, Aug. 12, 1941 (Dec. 21, 1938).—A process of producing an enamel frit comprises adding to the glassforming materials of the raw batch zirconium silicate and aluminum phosphate in such proportions that the mixture contains 7 to 15% zirconium silicate and 0.25 to 4% aluminum phosphate.

Glass

Absorption by protective glasses, especially of radiations of short wave length. T. GRAFF AND H. NAUMANN. *Blätter Untersuch.- & Forsch. Instrumente*, **13**, 24–31 (1939); abstracted in *Chem. Zentr.*, **1939, II**, 1944; *Chem. Abs.*, **35**, 4166 (1941).—Spectrographic investigations of Ultrasine glasses, of Hallauer gray-green protective glasses, and of gray and blue protective glasses are reported. Only the Ultrasine glasses and the gray-green protective glasses gave effective ultraviolet protection. Simple gray and blue glasses protected only against glare and afforded no ultraviolet protection.

Antiscattering treatment for windows. H. M. LLEWELLYN. *Chem. & Ind.*, **60** [23] 433–34 (1941).—Materials tested as antiscattering treatments applied to glass to reduce the danger of flying fragments included about 210 liquids and 220 adhesive nets. Reports are given of tests using liquid treatments, transparent films, textile fabrics, and a strip treatment. G.R.S.

Barium crown for fused bifocals. ANON. *Optician*, **101** [2606] 72 (1941).—Fused bifocals with segments of flint glass suffer from chromatic aberration. Barium glass would overcome this, but it has unusual physical properties which give rise to manufacturing problems. The difficulty of obtaining a pot in which to melt the batch is overcome by combining hard rugged clays (to give strength) with the finest clays (to render it porous). Instability of the glass to atmosphere and moisture is overcome by correct additions of boron, quartz, potash, lime, and traces of zirconium. Special precautions must be taken in the polishing and grinding operations, and special edging stones must be provided. M.B.H.

Bead makers and bead factories in Bohemia. JOSEF BLAU. *Glastech. Ber.*, **19** [3] 89–92 (1941). J.F.H.

Calculation of lens arrangements and form dimensions for grinding and polishing round optical parts. FRANZ KLEIN. *Glastech. Ber.*, **19** [3] 86–89 (1941). J.F.H.

Cause of changes in strength of quartz glass at higher temperatures. W. DAWIHL AND W. RIX. *Glastech. Ber.*, **18** [10] 265–67 (1940).—Strength measurements were made at room temperature and at 800°C. on strongly etched vitreous silica rods. The increase in strength with temperature was of the same order of magnitude as that of unetched rods, showing the absence of any effects due to surface changes. Tests at room temperature and at 800°C. showed that the strength increase is independent of the loading velocity. Measurements at 150°C. also showed proportionate increases in strength over that at room temperature. This is believed to be due to reversible atomic structure changes rather than to an effect on the flaws as pictured by Smekal. Strengths of 10, 12.2, and 13.4 kgm. per mm.^{2} were found at 25°, 150°, and 800°, respectively. See "Increasing. . .," *Ceram. Abs.*, **19** [6] 137 (1940). J.F.H.

Coloring bodies in the so-called carbon-yellow glasses: III, Coloring due to iron-sulfur compounds. C. NEUMANN AND A. DIETZEL. *Glastech. Ber.*, **18** [10] 267–73 (1940).—Iron and sulfur occur as FeS in relatively acid glasses under relatively strongly reducing melting conditions. In this form it imparts a grayish color that is distinctly colloidal and can be developed by heat treatment. The important carbon-yellow color is due largely to the sulfoferrite ion in true solution along with the polysulfide. The ferrite ion, in which the iron is trivalent, is formed more readily, the more basic the glass. Its formation is also favored by moderate reducing conditions during melting. To produce a good color, it is desirable to keep the base glass as alkaline as possible and the iron content low to avoid the formation of FeS which dulls the color. A red unstable colloidal color was encountered in acid glasses, caused possibly by the presence of Fe_2S_3. Absorption measurements show that sulfur in the form of polysulfide produces the least coloring effect. As ferrite, its effectiveness in causing color is ten times greater. The effect of FeS is one hundred times that of sulfur as polysulfide. For Part II see *Ceram. Abs.*, **19** [3] 62 (1940). J.F.H.

Damping of vibrations within materials. Discussion of "Acoustical properties of glass." HELMUT RÖTGER. *Glastech. Ber.*, **18** [12] 362–63 (1940); see *Ceram. Abs.*, **20** [3] 64 (1941). J.F.H.

Design of bottles that contain crystallizing liquids. F. W. PRESTON. *Glass Ind.*, **22** [7] 306–307, 315 (1941).—Products such as Rock and Rye often set up stresses in the container that cause breakage. Proper design of the basal part of the bottle can overcome this difficulty. For maximum strength with a minimum of glass (*a*) the bottle should be circular in cross section, at least in the lower parts; (*b*) the Murgatroyd belt should be rounded off into the base; (*c*) the sidewalls should be thicker near the base than near the shoulder; and (*d*) a moderate residual annealing strain will normally help. A.P.

Detection and determination of some rare glass constituents: II, Indium. W. GEILMANN AND E. STEUER. *Glastech. Ber.*, **19** [2] 40–43 (1941).—The spectrographic method is most suitable for the qualitative detection of indium. With a 0.1 gm. glass sample, 0.025% is detectable with certainty. Since aluminum does not interfere, it is advantageous in the case of small amounts to add 0.5 to 1.0 mgm. of aluminum as chloride to serve as a collector before precipitation with ammonia to concentrate it. While quantitative determinations can be made spectrographically after separation from accompanying interfering elements, the colorimetric determination as sulfide, the precipitation with 8-hydroxyquinoline, and electrometric titration with $K_4Fe(CN)_6$ are all satisfactory methods. For Part I see *Ceram. Abs.*, **19** [9] 212 (1940). J.F.H.

Determination of vanadium in glass using hydroxyquinoline. Z. SCHAEFER. *Glastech. Ber.*, **19** [3] 81–86 (1941).—Vanadium in the form of vanadate in a weak acetic acid solution can be precipitated with hydroxyquinoline. In glass analysis, the iron and the alumina are precipitated along with the vanadium. If vanadium alone is to be determined, Fe and Al can be removed after redissolving by the use of Na_2HPO_4, and the V can again be precipitated with hydroxyquinoline. For complete analysis, the Fe can be separated, using NaOH, and the Al can subsequently be separated by using Na_2HPO_4. When large amounts of Al are present, it is desirable to reprecipitate it with hydroxyquinoline and weigh as Al_2O_3. The glasses are best decomposed for analysis by the use of HF and HNO_3 with the addition of boric acid. Silica and alkalis must be determined on other samples. The method has been very useful on soda-lime (magnesia) glasses colored by iron and vanadium where the alumina has not been too high. J.F.H.

Economical pot and tank furnaces—gas generators. E. S. *Glashütte*, **71** [10] 157–59 (1941).—The first requirements for the economical operation of gas generators are that the five zones through which the fuel passes (drying, extracting, gasifying, combustion, and ash zones) be at a suitable height and that gasification be complete before the fuel enters the combustion zone; the height of the fire bed is the regulating factor, and it is better that it be placed too high than too low. The best heights for the fire bed for different fuels are listed, and the firing technique is described. The smaller the size of the fuel particles, the lower the fire bed should be. Uniformity of fuel grain size is important for complete gasification of fuels; smaller particles gasify more rapidly than larger particles. Different types of fuel should be burned separately unless they have a similar rate of gasification. The questions of draft and time and manner of removing the slag are also taken up. Loading must be done as quickly as possible to prevent the escape of gas where automatic chargers are not used. Misunderstanding of these particulars, not negligence, is usually responsible for the mismanagement of generators. See *Ceram. Abs.*, **20** [5] 114; [7] 176 (1941). M.V.C.

Electrochemical measurement of the partial pressure of oxygen in glass melts: II, Investigation of oxidation equilibria. PAUL CSAKI AND ADOLF DIETZEL. *Glastech.*

Ber., **18** [3] 65–69 (1940).—Using the potentiometric method described in Part I (*Ceram. Abs.*, **19** [10] 233 (1940)), the authors studied the Cr_2O_3-CrO_3 and the MnO-Mn_2O_3 equilibria in glasses. Spectrophotometric measurements again served to determine the ion percentages in the two states of oxidation. The chromium (0.1%) was introduced into the borax as $K_2Cr_2O_7$. Melts were made in oxygen, air, nitrogen, and a nitrogen-hydrogen mixture. The manganese was introduced into the manganese glasses as $MnCO_3$ except in one case in which $KMnO_4$ was used to raise the partial oxygen pressure as high as possible. The glasses were usually melted at 900°C., 3 hr. being sufficient to reach equilibrium conditions. The results are best presented by plotting the percentage of ions in the higher oxidation state against the potential measurements. They show that the order of increasing tendency to dissociate is as follows: Fe, Cr, Mn. The curves show clearly the amounts of iron, chromium, and manganese ions in various states of oxidation that may be present simultaneously under given melting conditions, e.g., small amounts of FeO are stable in the presence of certain amounts of CrO_3. To maintain more than 75% of manganese as Mn_2O_3 in a glass would require unusual oxidizing conditions. A borax melt containing 1% CeO_2 gave initially a negative potential (high oxygen partial pressure) and, after 25 min., became constant at +0.09 volt, thus showing how the strong tendency of the Ce_2O_3 to reoxidize lowered the partial oxygen pressure of the melt. Such studies are of importance not only in the melting of colored glasses but also in fining operations. J.F.H.

Fiber glass. S. BATESON. Read before Ottawa Section, Society of Chemical Industry, Jan., 1941; abstracted in *Chem. & Ind.*, **60** [18] 341 (1941). G.R.S.

Flexibility the keynote of new Brockway plant. ANON. *Glass Ind.*, **22** [7] 295–302 (1941).—At Plant No. 2 of the Brockway Glass Co., Inc., at Crenshaw, Pa., novel engineering features have been introduced to provide for future expansion without costly changeovers. 25 photographs and drawings of factory layout and batch house. A.P.

Glassware for the laboratory. J. J. MORAN. *Science Counselor*, **7**, 42–45, 61–62 (1941); *Chem. Abs.*, **35**, 4637 (1941).—M. discusses the American glass industry, the chemical composition of types of glass, and American production methods of making glass and chemical glass apparatus.

Glassware rejects cut 25% by building longer tank. ANON. *Ceram. Ind.*, **36** [6] 43–44 (1941).—The glass tank at Aladdin Industries, Inc., is built larger than usual to give a longer firing time which results in clearer glass and fewer rejects. The tank, 10 x 25 ft. in the melting chamber, is direct fired and is used for the firm's lamp-chimney requirements. H.T.

Glass wool as an insulation material. B. SÄRNÖ. *Tek. Tid.*, **70** [22] Elektrotek. 89–94 (1940).—S. describes the manufacture of glass wool and reviews the available information on its properties. Two types of glass wool are produced: (1) staple length fiber, which is made in lengths of 200 to 400 mm. with a thickness of about 0.006 mm., and (2) continuous fiber, which is about 0.005 mm. thick and is made in lengths limited only by the capacity of the bobbin on which it is wound. R.A.R.

Hardness behavior of glasses on grinding with a rotating grinding disk. KURT V. STOESSER. *Glastech. Ber.*, **18** [12] 337–53 (1940).—The samples, 3-cm. squares, were cemented to one pan of a balance directly under the cutting surface of the grinding wheel so that a constant pressure, usually a 500-gm. load, was maintained at the point of contact. The cutting wheel was 2.8 cm. in diameter and was motor driven with controlled speed so that calculation of the distance of travel of the cutting surface was possible. Losses in weight of both the samples and cutting disks were determined, and precautions were taken to keep the cutting disk surfaces uniform. Cutting disks of silicon carbide, corundum, and various glasses were tested against samples of window glass and various optical glasses. The volume of glass removed was found to be directly proportional to the distance of travel of the cutting surface and to the load for constant distance of travel. With increasing velocity, however, the volume of glass removed increased rapidly to a fairly sharp maximum and then gradually decreased. This behavior appears to be due to the fact that the softening temperature of the glass is reached at the velocity corresponding to this maximum. A comparison of the transformation and softening temperatures with the critical velocities for some of the glasses tends to confirm this view. Different hardness series for the glasses result from using various cutting disks. This is due to a number of factors, such as the thermal properties and the coefficient of friction of the materials in contact. In some cases it is even possible that a eutectic melt may be formed at the point of contact. The ratio of volume loss of the cutting disk to volume loss of the plate gives a reproducible value for the relative hardness of the two materials, but it is strongly dependent on the velocity. At lower velocities for the same time, a smooth cutting disk in some cases removes more glass than the bonded abrasive disks. J.F.H.

Hygrade Sylvania's low-expansion alloy for glass-to-metal seals. W. E. KINGSTON. *Tech. Horizons* [Supp. to *Steel Horizons*], **3** [1] 1–12 (1941); *Chem. Abs.*, **35**, 4927 (1941).—From a study of about 65 Fe-Cr, Fe-Ni, Fe-Ni-Cr-Co, Fe-Ni-Cr, Fe-Ni-Cr-C, Fe-Ni-Si, Fe-Ni-Cr-Si, Fe-Ni-Mo, Fe-Ni-Cr-Al, and Fe-Ni-Al alloys, there was developed a series of Fe-Ni-Cr alloys (with small amounts of other elements) particularly suitable for vacuum-tight glass-to-metal seals. By varying the principal constituents of these alloys, coefficients of expansion ranging from 70 to 120 $\times 10^{-7}$ per degree can be obtained. They are well suited for seals to glass where great mechanical stresses are encountered. Thermal-expansion curves for various glasses and alloys are shown.

Influence of inner strains in glass on its stability toward thermal shock. MILOTA FANDERLIK. *Glastech. Ber.*, **18** [11] 314–20 (1940).—The test pieces were carefully selected 5- x 30-mm. rods with fire-polished ends. Three glasses with expansions of 102.9 $\times 10^{-7}$, 52.8 $\times 10^{-7}$, and 42.4 $\times 10^{-7}$ were used. Some of the rods were annealed, and other sets were treated by being heated to the softening temperature and to 5°, 10°, 15°, and 20° below the softening temperature and dropped into a chilling bath of tallow and mineral oil heated to 150°, 200°, and 250°. The test pieces were then sorted into groups by examination in a strain tester with the aid of a compensator, and the strain was expressed as the phase difference in millimicrons for a 5-mm. thickness. The resistance to thermal shock was determined in the usual way by quenching from various temperatures. The amount of breakage during tempering of the samples was lowest with the glasses heated to their softening temperature. In all cases, the resistance to thermal shock increased with increasing internal strain. The average thermal resistance for a phase difference of 400 mμ increased from 123° to 220°, from 194° to 328°, and from 220° to 354° for the high-, medium-, and low-expansion glasses, respectively. For strain-free glass, the lower the expansion, the greater is the thermal resistance. Chilling also gives a higher absolute thermal stability in glasses already thermally resistant without strain. The relative increase in resistance, however, is greater with less resistant glasses (assuming the same degree of strain). J.F.H.

Influence of magnesia on the devitrification constants of soda-lime glasses. A. DIETZEL. *Glastech. Ber.*, **19** [2] 43–46 (1941).—The crystal-melt equilibria were examined for soda-lime glasses of the composition 74 SiO_2, 12 to 18 Na_2O, and 8 to 14% CaO with systematic replacement of CaO with MgO. A galvanometer and photocell combination was used for temperature control. The results are presented graphically by plotting velocity of crystallization against temperature. The crystallization velocity decreases about 10% for each per cent of MgO added. The main crystal phases encountered were devitrite and cristobalite or tridymite. In the lower temperature range, the slowly crystallizing diopside, CaO·MgO·$2SiO_2$, and akermanite, $2CaO·MgO·2SiO_2$, were observed. In the 16% Na_2O glass, replacement of the CaO with MgO

beyond 8% results in two new soda-magnesium silicate crystal phases, whose optical properties are described. See *Ceram. Abs.*, **18** [4] 97 (1939). J.F.H.

Investigation of glass surface by means of reflection measurements. HANS FREYTAG. *Glastech. Ber.*, **19** [2] 50–54 (1941). J.F.H.

Ion exchange on glass surfaces. B. VON LENGYEL AND J. VINCZE. *Glastech. Ber.*, **18** [10] 273–75 (1940).—Glasses useful for glass electrodes are of two types, depending on their electrical behavior. Glasses of the first type are free of B_2O_3 or Al_2O_3 and give potentials that are an exact measure of the hydrogen-ion concentration in the pH range 0 to 9 independent of other cations. Glasses containing suitably over 10% of Al_2O_3 or B_2O_3 lose their sensitivity to the hydrogen ion in neutral or alkaline solution, and their potential becomes a function of the Na^+ concentration. By using the two types of electrodes in conjunction with silver-silver chloride electrodes and with the powdered test glass immersed in 0.0001 HCl, it is shown that the H^+-Na^+ exchange on the glass surface is quantitative. J.F.H.

Light conditioning. EDWIN TEALE. *Popular Science Monthly*, **139** [1] 73–76 (1941).—New developments of the glass industry which enable architects and builders to control and direct daylight are (1) Thermolux, formed of two sheets of clear glass with woven spun glass hermetically sealed between them, (2) infrared-absorbing glass, (3) water-white plate glass, (4) light-directional glass blocks, (5) metal framework for setting glass blocks, (6) V-shaped corners to strengthen the bonding of glass blocks, (7) fused-glass designs to give glass blocks decorative effects similar to those of stained glass, and (8) blackout for factories by the use of sodium lights with blue windows. Illustrated. A.P.

Lighting principles and practice with glass-block panels. D. A. BRIDGES. *Eng. News-Record*, **127** [1] 65 (1941).—Daytime lighting of buildings with panels of glass block requires a knowledge of their properties and methods of installation. Prismatic blocks are so designed that sunlight may be refracted from any altitude position of the sun toward the ceiling. This principle permits more light to be directed deeper into the room than is possible with ordinary window glass. Wall panels are erected with mortar joints using a reinforcing of wire mesh. Expansion is provided for by a filler in chases at the head and sides. Large panels require stiffeners or mullions. B.C.R.

Melting and working of quartz glass and similar high-melting glasses. WALTER HÄNLEIN. *Glastech. Ber.*, **18** [11] 308–14 (1940).—The development of the high-pressure mercury arc has required the production of larger quantities of tubing with more exacting dimensions at a lower cost. H. reviews the developments in this field and describes a new procedure using a molybdenum crucible and nozzle. See "Continuous . . .," *Ceram. Abs.*, **20** [1] 11 (1941). J.F.H.

Microanalytical test procedures for the investigation of glasses. M. NIESSNER AND F. KORKISCH. *Glastech. Ber.*, **19** [2] 33–39 (1941).—Microanalytical procedures for the detection and qualitative separation of Co, Ni, Mn, U, Cr, Fe, Cu, Au, Se, and Ce are presented in detail. The procedures were chosen on the basis of simplicity and speed. To avoid errors, the effect of interfering elements has been examined in individual tests. The tests were carried out on glass samples to determine the limits of accuracy in the presence of other elements. The glass to be tested was treated with HF and mineral acid to dissolve approximately 20 mgm., and the tests were then carried out with drops on a spot plate or filter paper. J.F.H.

Microscopic examination for control in the manufacture of spectacle lenses. H. FESEFELDT AND T. GRAFF. *Glastech. Ber.*, **19** [2] 55–57 (1941). J.F.H.

Optical glass. HANS SCHULZ. *Glastech. Ber.*, **19** [2] 57–61 (1941).—The index of refraction and the dispersion of Jena glasses are plotted against density. Further calculations used in the selection of optical glasses are presented. See *Ceram. Abs.*, **19** [5] 111 (1940). J.F.H.

Polarization of the light passing through opal glass. I. MROZOWSKA. *Rocznik Akad. Nauk Tech. Warszawie*, **4**, 234–41; abstracted in *Chem. Zentr.*, **1939, II**, 1438–39; *Chem. Abs.*, **35**, 3903 (1941).—The degree of polarization of the light passing through the opal glass was measured for different angles of incidence and from different directions of observation. In the different series of experiments the incident light was unpolarized or polarized in the plane of incidence or in the plane perpendicular to it. Glass plates of different thicknesses were used which had been matted by either chemical or mechanical means. The experimental results are reported in graphs and tables.

Potassium carbonate in glassware. ANON. *Ceram. Ind.*, **36** [4] 96–98 (1941).—The use of potassium carbonate in glassware is described briefly, and its advantages and disadvantages are compared with those of soda. The advantages are greater brilliance, a more bell-like ring, and improved coloring and acid-etching effects. The disadvantages are a higher batch cost, need of a longer fining time, and more rapid tank corrosion and, therefore, more stone defects in the ware. H.T.

Preliminary note on the chemical mechanism of decolorizing with selenium. FRANK DAY, JR., AND ALEXANDER SILVERMAN. *Jour. Amer. Ceram. Soc.*, **24** [9] 297 (1941).

Progress being made in Fiberglas. GAMES SLAYTER. *Fibre & Fabric*, **94** [2920] 10–11 (1941); *Chem. Abs.*, **35**, 4166 (1941); see *Ceram. Abs.*, **20** [2] 41 (1941).

Rapid method for determining the opacity of glasses to the near ultraviolet. W. R. LESTER. *Glass Ind.*, **22** [7] 305 (1941).—The glass to be tested is placed between an ultraviolet light source and a fluorescent material, and the residual degree of fluorescence is compared arbitrarily with that obtained with filters having known cutoffs. A 0.1% solution of quinine sulfate in water, acidified with a few drops of sulfuric acid, is satisfactory for the fluorescent material. A.P.

Resistance of glass to abrasion. N. P. PODKOPAEV AND V. P. USPENSKII. *Trudy Ivanov. Khim. Tekh. Inst.*, **1940**, No. 3, pp. 153–57; *Chem. Abs.*, **35**, 3047 (1941).—Glass samples of various compositions were tested for their chemical stability and their resistance to abrasion. Hooks made from these glass samples were tested for their suitabillity for use in the manufacture of artificial thread. Hooks made of glass consisting of SiO_2 72, B_2O_3 8.15, CaO 1.55, MgO 0.45, Na_2O 7.2, and K_2O 10.45% lasted only two days, while hooks made of glass consisting of SiO_2 73, Al_2O_3 2.5, Fe_2O_3 0.5, CaO 12.0, and Na_2O 12% lasted 13 days. The chemical stability and resistance to abrasion of glass is a function of the chemical composition. 18 references.

Safety glass. R. RICHARDSON. Read before Ottawa Section, Society of Chemical Industry, Jan., 1941; abstracted in *Chem. & Ind.*, **60** [18] 341 (1941). G.R.S.

Sand grain size and the SO_3 content of glass. JOSEF REIL. *Glastech. Ber.*, **18** [3] 75–76 (1940).—The SO_3 content of a glass is found to depend somewhat on the grain-size distribution of the sand. J.F.H.

Sealing tests on conserve glasses. G. SCHIKORR AND I. RAKEBRAND. *Glastech. Ber.*, **19** [2] 47–50 (1941). J.F.H.

Selection of glasses for optical uses. HANS SCHULZ. *Glastech. Ber.*, **18** [11] 320–21 (1940).—The available optical glasses are plotted on an index of refraction-dispersion diagram. Curves are drawn for the case $\nu_1 = 60$, and the initial index values are 1.5, 1.55, and 1.6. This shows the areas where glasses of desirable optical properties are lacking. Equations are presented for making the required calculations in selecting glasses. J.F.H.

Significance of the basicity of glass melts and the investigation of its measurement: I. W. STEGMAIER AND A. DIETZEL. *Glastech. Ber.*, **18** [11] 297–308 (1940).—Experimental data are gathered from the literature indicating the desirability of considering the glassmelting operation as a solvent action of the glassforming oxide rather than as salt formation from an acid and base. The oxygen-ion concentration is proposed as a measure of the "basicity" of glasses. Soda and potash glasses of the silicate, borate, and phosphate systems were considered. Melts were made at 1100° in a small platinum drum rotated in an electric furnace around a horizontal axis, and pre-

cautions were taken to attain equilibrium with the atmosphere. Chromic oxide, vanadium pentoxide, manganese oxide, and iron oxide, in small amounts, were used as color indicators, and the color changes were determined with the systematic change in alkali concentration. With 2% Fe_2O_3 as indicator in the series lithium, sodium, and potassium borates, 17, 12, and 8 mol %, respectively, of the bases were required to give an extinction coefficient of 0.21 for a thickness of 4 mm. The behavior of the other indicators was not satisfactory in all cases. With the series sodium silicate, borate, and phosphate, 15, 36, and 65 mol % of the bases were required for color change with CrO_3 as indicator. The results were similar with V_2O_5. This agrees with the generally accepted order of increasing acidity for the glassforming oxides SiO_2, B_2O_3, and P_2O_5. **II.** *Ibid.*, [12] 353–62.—To study further the suitability of oxygen-ion concentration as a measure of basicity, electrometric measurements were made on Li, Na, and K borate glasses, using the following cell arrangements: +Pt (air) | borate melt, 0.5 to 0.7% R_2O || borate melt, x% R_2O | Pt (air) —; and +Pt (air) | B_2O_3 || borate melt, x% R_2O | Pt (air) —. The measurements were made at 850°C. in a hard porcelain or corundum crucible 35 mm. high with a top diameter of 41 mm. and a bottom diameter of 20 mm. A partition through the middle separated the two melts. The Pt electrodes were immersed to a depth of 2 mm. With this arrangement, equilibrium was readily attained in 10 to 15 min. to give satisfactorily reproducible e.m.f. measurements. When the mol per cent of alkali is plotted against potential, the point of maximum change in slope occurs near 20 to 22% alkali, with the curve for potassium borate showing the greater change and the lithium borate giving the flattest curve. In a comparison test using sulfur (added as Na_2S) as indicator, the color change from brown (base) to blue (acid) for the K, Na, and Li borates occurred at 25.5, 27.5, and 36.5%, respectively. These values correspond to the same value of 0.83 volt on the three potential-composition curves. The higher potential for the lithium glass at low alkali concentration is interpreted as showing that the basicity is reversed so that the potash glass is the most acid. Experiments using cobalt oxide as indicator agree with this. This may be due to the greater mobility of the Li^+ in the more rigid lattice. The calculation of absolute oxygen-ion concentrations is not yet possible, because of the possibility of diffusion potentials in the field of lower alkali content and because of lack of knowledge about the oxygen-ion concentration for B_2O_3. With increasing alkali content, the potential curves approach a maximum limiting value which apparently at the same time corresponds to the neutral point between acids and bases. All of the ordinary glasses, accordingly, are in the acid region, and disilicates or tetrasilicates can be formally considered as acid salts. J.F.H.

Streaked glass—evolution of the term "streaks." L. Springer. *Glashütte*, **71** [11] 169–70; [13] 194–95 (1941).—A reference list of old and recent publications on streaks in glass is given with a few words of explanation of each article. The original meaning of the term and the changes gradually made in it are explained. The definition of the technical term, "streaks," finally adopted is as follows: "A streak is a distortion or dispersion of light or other color in the glass mass, which also emerges under certain conditions on the surface as a different coloring or in the form of a perceptible constituent of the mass, especially of oblong or flat form and indefinite outline." M.V.C.

Strength properties of glass. Hans Joachim Krug. *Glastech. Ber.*, **18** [3] 70–74 (1940).—The results are in agreement with those of earlier workers. J.F.H.

Surface tension of glasses: III. Gustav Keppeler and Alfred Albrecht. *Glastech. Ber.*, **18** [10] 275–80 (1940).—For a series of glasses used for the manufacture of blown ware, surface tensions between 270 and 301 dynes per cm. at 1370°C. were found. The temperature coefficient for these glasses was small (between 0.018 and 0.094). Replacement of Na_2O by K_2O up to 10% causes a marked rise in surface tension, which again drops on further replacement. For commercial flat glasses, values of 290 to 302 dynes per cm. were found. Since the ratios of surface tension to viscosity are small, with a maximum value of 1.3 at 1370°C., it is concluded that the surface tension is not an important factor in most fabrication operations. Surface-tension measurements using CO_2 and SO_2 gave the same values as air, so that any improvement in fining by the addition of sulfate cannot be ascribed to surface-tension effects. For Parts I and II see *Ceram. Abs.*, **20** [3] 66 (1941). J.F.H.

PATENTS

Apparatus for casehardening glass plates. William Owen (Pittsburgh Plate Glass Co.). U. S. 2,251,160, July 29, 1941 (Oct. 14, 1938).

Apparatus for casehardening glass sheets. L. V. Black and G. Z. Minton (Pittsburgh Plate Glass Co.). U. S. 2,251,106, July 29, 1941 (May 18, 1938).

Apparatus for glass manufacture. J. F. Byers (Libbey-Owens-Ford Glass Co.). U. S. 2,252,756, Aug. 19, 1941 (July 16, 1937).

Apparatus for manufacture of foliated glass. E. H. Wellech and W. C. Weber (Corning Glass Works). U. S. 2,251,727, Aug. 5, 1941 (May 25, 1937; Feb. 18, 1938).

Apparatus for stacking glassware. H. A. Wadman and A. J. Smith (Hartford-Empire Co.). U. S. 2,253,155, Aug. 19, 1941 (March 27, 1939).

Coating composition for molds. E. H. Haux (Pittsburgh Plate Glass Co.). U. S. 2,251,130, July 29, 1941 (May 17, 1938).—A glassforming mold comprises inner walls of refractory material for containing melted glass to be molded therein, the inner wall sides having painted thereon a coating applied in the form of an aqueous suspension which, when dry, is nonadherent to melted and molded glass and containing approximately 2 to 50% by weight of yellow ocher.

Device for measuring flatness of glass. C. M. Tuttle and R. V. Cartwright (Eastman Kodak Co.). U. S. 2,253,054, Aug. 19, 1941 (Sept. 13, 1939).

Fining glass and batch therefore. A. K. Lyle (Hartford-Empire Co.). U. S. 2,252,131, Aug. 12, 1941 (July 1, 1939).—A batch composition for a clear, colorless, transparent glass of the soda-lime type comprises a material containing tellurium and a sufficient amount of a material selected from the group consisting of arsenic and antimony oxides to prevent the tellurium from discoloring the glass.

Glass-blowing machine. J. P. Benoit, R. G. Allen and L. H. Wideman (Owens-Illinois Glass Co.). U. S. 2,252,391, Aug. 12, 1941 (Dec. 17, 1938).

Glasses containing lead. General Electric Co., Ltd., A. L. Marden, and J. H. Partridge. Brit. 537,855, July 23, 1941 (Aug. 30, 1940).

Glass feeding. Peter Kucera. U. S. 2,250,110, July 22, 1941 (Nov. 9, 1939).

Glass-feeding apparatus for rolling machines. Joseph Gaskell (Pilkington Bros., Ltd.). Can. 397,677, July 1, 1941 (July 11, 1939). G.M.H.

Glass-feeding device. T. H. Jeffers. U. S. 2,253,277, Aug. 19, 1941 (Dec. 8, 1939).

Glass filament producing apparatus. Armand Lamesch. Can. 398,036, July 15, 1941 (Sept. 17, 1937). G.M.H.

Glassforming apparatus. E. H. Wellech (Corning Glass Works). Can. 398,126, July 22, 1941 (June 27, 1939; in U. S. July 16, 1938). G.M.H.

Glass gathering and molding apparatus. J. H. Williams. U. S. 2,250,515, July 29, 1941 (Oct. 2, 1937).

Glass of high softening point. Walter Hänlein (General Electric Co.). U. S. 2,252,466, Aug. 12, 1941 (Sept. 10, 1938).—A glass having a softening point at least as high as 1000°C. consists, by weight, of 90 to 94% silica, 3 to 5% alumina, 1.5 to 2.5% of an oxidic component selected from the class consisting of one or more alkaline-earth oxides and mixtures of beryllium oxide and one or more alkaline-earth oxides, and 1 to 3% of another oxidic component selected from the class consisting of zirconium oxide, thorium oxide, and mixtures of zirconium oxide and

thorium oxide, the total amount of alumina plus the amount of the second oxidic component not exceeding substantially three times the amount of the first oxidic component.

Glass machine. J. A. LEWIS (Sneath Glass Co.). U. S. 2,251,847, Aug. 5, 1941 (Nov. 5, 1938).

Glassmaking. J. B. WHITMORE AND F. A. NEWCOMBE (Westinghouse Electric & Mfg. Co.). U. S. 2,252,589, Aug. 12, 1941 (Sept. 1, 1939).

Glassmelting tanks. CORNING GLASS WORKS. Brit. 537,429, July 2, 1941 (April 22, 1939).

Glass-pressing machine. T. H. JEFFERS. U. S. 2,253,276, Aug. 19, 1941 (Aug. 30, 1938).

Glass-shearing mechanism. J. P. BENOIT, R. G. ALLEN, AND L. H. WIDEMAN (Owens-Illinois Glass Co.). U. S. 2,252,392, Aug. 12, 1941 (Feb. 16, 1939).

Glass sheet coating apparatus. C. S. SHOEMAKER (American Window Glass Co.). Can. 398,078, July 22, 1941 (Aug. 12, 1939; in U. S. April 26, 1939). G.M.H.

Glass-tempering apparatus. J. B. MITFORD AND W. W. SHAVER (Pilkington Bros., Ltd.). Can. 397,678, July 1, 1941 (Oct. 23, 1939). G.M.H.

Glass tempering apparatus timing mechanism. A. W. WEBER (Corning Glass Works). Can. 396,501, May 13, 1941 (March 31, 1939; in U. S. May 21, 1928). G.M.H.

Glassware forming machine. R. G. ALLEN (Owens-Illinois Glass Co.). U. S. 2,251,010, July 29, 1941 (April 21, 1939).

Glass wool blowing apparatus. H. C. BATES (Fiberglas Canada, Ltd.). Can. 398,130, July 22, 1941 (Feb. 8, 1938; in U. S. March 30, 1937). G.M.H.

Lehr loader. F. C. LINK AND W. E. LINK. U. S. 2,252,937, Aug. 19, 1941 (Aug. 25, 1937).

Lens-edging machine. E. M. LONG (Shuron Optical Co., Inc.). Can. 398,015, July 15, 1941 (May 29, 1939). G.M.H.

Low-reflectance glass. BRITISH THOMSON-HOUSTON CO., LTD. Brit. 537,591, July 9, 1941 (April 28, 1939).

Manufacture of foliated glass. E. H. WELLECH AND W. C. WEBER (Corning Glass Works). U. S. 2,251,726, Aug. 5, 1941 (May 25, 1937).

Manufacture of glassware. BRITISH HARTFORD-FAIRMONT SYNDICATE, LTD. Brit. 537,795, July 16, 1941 (March 17, 1939). Brit. 537,796, July 16, 1941 (March 27, 1939).

Method and apparatus for melting and fining glass. GAMES SLAYTER (Owens-Corning Fiberglas Corp.). U. S. 21,863, July 22, 1941 (Jan. 9, 1941); reissue of original U. S. 2,212,528, Aug. 27, 1940 (Dec. 28, 1935).

Mortar-bonded glass structure. R. R. MCGREGOR AND E. L. WARRICK (Corning Glass Works). Can. 397,620, July 1, 1941 (Feb. 9, 1940; in U. S. April 18, 1939). G.M.H.

Oil-treated mineral wool. W. V. CULLISON (American Rock Wool Corp.). U. S. 2,252,169, Aug. 12, 1941 (Aug. 14, 1939).

Process and apparatus for bending and tempering glass sheets. WILLIAM OWEN (Pittsburgh Plate Glass Co.). U. S. 2,251,159, July 29, 1941 (Dec. 9, 1936).

Production of decorative glass. W. O. LYTLE (Pittsburgh Plate Glass Co.). U. S. 2,251,144, July 29, 1941 (April 14, 1938).

Rotary electric furnace. JOHN FERGUSON. U. S. 2,250,155, July 22, 1941 (May 13, 1940).

Rotary glassware forming machine. C. C. KINKER (O'Neill European Machine Co.). Can. 397,674, July 1, 1941 (Jan. 27, 1940). G.M.H.

Sealing glass making method. R. H. DALTON AND M. E. NORDBERG (Corning Glass Works). Can. 398,279, July 29, 1941 (April 1, 1940; in U. S. April 22, 1939). G.M.H.

Shaping of glass sheets. L. J.-B. FORBES (Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St.-Gobain, Chauny & Cirey). U. S. 2,250,628, July 29, 1941 (Sept. 16, 1936).

Structural Clay Products

Brick traffic markers in Baltimore. W. P. FANNING. *Dependable Highways*, No. 171, pp. 5–8 (1941).—Various designs and types of marker construction are described in detail and illustrated. P.S.D.

Cleaning cutter wires with steel brushes reduces wear and costs. C. F. GREENE. *Brick & Clay Record*, **93** [6] 30 (1938).—In the manufacture of ladle brick, corners and edges should be as perfect as possible. Wire cutting of the $2^1/_2$-in. dimension produced better sized brick than could be obtained by re-pressing. Because of the difficulty of keeping the wires clean, steel wire brushes fastened to an automatic cutter were utilized for this purpose. B.C.R.

Effect of lime additions on the properties of green and fired brick. YA. A. SOKOLOV. *Prom. Stroitel. Materialov*, **2** [8] 43–45 (1940).—The addition of lime to clay lowers the mechanical strength of ordinary brick. The addition should not exceed 0.3% of the weight of the batch. P.B. & E.S.

Efflorescence of brick. A. SIMON AND R. MEIER. *Ziegelwelt*, **72**, 51–55 (1941); *Chem. Abs.*, **35**, 4927 (1941).—$CaSO_4$ dissociates rapidly at 750° to 900° in the presence of kaolin, while clays containing appreciable amounts of $CaCO_3$, $MgCO_3$, Fe_2O_3, and alkalis tend to regain and retain SO_3 from the combustion gases at higher temperatures. Reducing atmospheres tend to decrease the amounts of efflorescence salts in the fired brick. The temperature range of maximum sulfate formation is 600° to 800°. The concentration of sulfates is greatest in the outer 1 mm. of the brick, with decreasing amounts at 2- to 5-mm. depths. Additions of Fe_2O_3 up to 5% increase the building of sulfates in brick fired in sulfurous atmospheres.

Influence of the composition of the water used for mixing on the properties of the body. JOSEF MATĚJKA. *Stavivo*, **20**, 280–85 (1939); abstracted in *Chem. Zentr.*, **1939, II**, 3865; *Chem. Abs.*, **35**, 5267 (1941).—Test brick were made from four different kinds of clay, using the water of the brickyard and distilled water. The drying shrinkage was greater when industrial or tap water was used. Tests on the fired brick showed that hard water lowered the fusion point of easily fused clays. The tendency to effloresce increased at a definite firing temperature (cone 010a). Brick fired at a high temperature showed lower absorptive capacity.

Large clay units. ANON. *Brick & Clay Record*, **96** [5] 18–21 (1940).—A survey among manufacturers on the relative merits of large sized clay units brought out the following points: (1) large units lower production costs and permit fairer competition with concrete and cinder block; (2) large units have helped to regain business in foundation work; (3) large units must be easily handled; a one-hand block with a handle feature is preferred; (4) the 5 x 8 unit is the most popular although the 8 x 12 and 12 x 12 sizes may have possibilities; (5) contractors and bricklayers favor the larger units; (6) only in certain localities have large units penalized bricklaying production. B.C.R.

Marker brick installations in New York. ANON. *Dependable Highways*, No. 171, pp. 9–10 (1941). P.S.D.

Modular design. ANON. *Architectural Forum*, **75** [1] 31–34 (1941).—Project A62 of the American Standards Assn., sponsored by the American Institute of Architects, has resulted in the coordination of dimensions long sought after by individual architects, prefabricators, and manufacturers of masonry materials, especially clay products. In its two years of existence it has developed on a 4-in. increment a simplified brickwork, backup tile, cast stone, concrete block, and the many details of millwork. A basic method to be applied by the architect to many other materials for any type of construction or design has been perfected. A brief account of the application of this

method to light construction in brick or frame is outlined in a plan using brick veneer, which is more complicated than frame or solid masonry. Nominal and actual dimensions, joist lengths, and stud spacing with the 4-in. nominal units coordinated under this principle result in lowered cost and improved appearance. Illustrated. M.E.P.

Mud huts to skyscrapers. NEILSON C. DEBEVOISE. *Sci. Amer.*, **164,** 340–42 (1941).—Sun-dried mud brick has always been the most common building material in the Near East. By 2700 B.C. simple bonding and, occasionally, English bond were used, sometimes with reed reinforcements between the courses. Fired brick were expensive and were used only when water made them necessary. Bitumen was used as waterproofing and in mortar. Plans for buildings were cut into stone or clay. Flat mud roofs were held up by poles. Arches with a span up to 35 ft. were used after 2700 B.C. They were usually erected without centering by leaning them against a heavy wall at one end. The barrel vault, dome, and arch were developed at about the same time in Mesopotamia. Columns appeared as early as 3400 B.C. W.D.F.

Prefabricated structural clay tile floor system. E. F. WANNER. *Bull. Amer. Ceram. Soc.*, **20** [8] 276–80 (1941).—4 references, 4 figures.

Reinforced brick paving slabs possess high load capacity. ANON. *Brick & Clay Record*, **92** [1] 15–16 (1938).—Blocks 8 x 8 x $3^1/_2$ in. are laid in a sand cushion and reinforced with longitudinal and transverse steel bars placed in every joint. The vertical sides of the blocks have lugs to support the reinforcing bars. A cement-sand grout is broomed or luted into the joints. Tests indicate that this type of construction is cheaper and stronger than the present type. B.C.R.

Salt-glazed brick. ANON. *Brick & Clay Record*, **96** [6] 24–25 (1940).—Plant operations for making salt-glazed brick are described. B.C.R.

Second-hand brick. ANON. *Brick & Clay Record*, **93** [1] 21–24 (1938).—The use of used brick for exterior purposes should be discouraged because of their tendency to disintegrate, effloresce, and become leaky due to failure of the mortar to bond properly. B.C.R.

Speed of auger affects quality of ware. J. G. SEANOR. *Brick & Clay Record*, **97** [1] 20–21, 30 (1940); reprinted in *Brit. Clayworker*, **49** [582] 151–53 (1940).—Factors affecting the operation of an auger machine include machine and auger design, uniformity of raw material, grinding, feeding of clay, pugging, auger speed, and the type of die used. Weaving of the clay column may be reduced by increasing the number of auger wings. With deairing machines, it is better to pug softer than was the practice before deairing and to depend upon the vacuum to give the clay its desired hardness. Cases in which stiffer pugging must be resorted to in order to maintain the vacuum can be corrected by the use of a new sealing die. B.C.R. + R.A.H.

Testing the resistance to frost of brick products. A. MÖSER. *Ziegelwelt*, **71,** 229–32 (1940); abstracted in *Chem. Zentr.*, **1940, II,** 2071.—M. discusses the resistance to frost of building materials. He suggests the possibilities of certain parallels which appear in the testing of refractory products for stability to temperature change. In the consideration of a better method for determining the resistance to temperature change, the function of the permeability is referred to as an indication of the structure and also of the behavior toward frost. After mentioning different processes for determining the values for permeability, methods are suggested for the better evaluation of the present freezing test and also for further elucidation of the properties important for stability to the action of frost. M.V.C.

PATENTS

Brick unit handling fork. HENRY PRIESTER. U. S. 2,250,273, July 22, 1941 (Sept. 14, 1940).

Design for building block. ERNST STEINHARD (Marley Tile Co., Ltd.). U.S. 128,811, Aug. 12, 1941 (May 20, 1940).

Process and apparatus for the manufacture of profiled brick. VIKTOR EHRENHAFT. U. S. 2,250,576, July 29, 1941 (Aug. 19, 1939).

Refractories

Argillaceous rocklike refractory materials of the U.S.S.R. F. A. ZENKOVICH. *Ogneupory*, **8** [11–12] 590–603 (1940).—Large deposits of rocklike refractory materials, similar to American flint clay, located in Soviet Russia are described. M.V.C.

Corundum refractories for lining the sintering zone of rotary cement kilns. M. A. FRAÏFELD. *Ogneupory*, **8** [5–6] 265–71 (1940); see *Ceram. Abs.*, **20** [7] 169 (1941). M.V.C.

Crucibles for the fusion of aluminum and aluminum alloys. M. FELICI. *Giornale Chimici*, **33,** 173–74, 179–80 (1939); abstracted in *Chem. Zentr.*, **1939, II,** 2706; *Chem. Abs.*, **35,** 5078 (1941).—A report is given of the comparative behavior of the various materials used for the manufacture of crucibles for the fusion of Al. The rapid wearing out of these crucibles is due to the high reactivity of Al in the molten condition. This can be greatly reduced if care is taken in the choice of materials for crucibles and in the preliminary treatment to prevent the transference of the electronic charge from the Al to the crucible material and conversely. This is accomplished, e.g., by (1) heating the bauxite to about 1350° for the purpose of very complete dehydration; (2) the use of graphite with the highest possible C content; (3) the addition of kyanite previously heated to 1450°, of andalusite preheated to 1550°, of sillimanite + clay or of sillimanite + MgO + artificial spinel, of technically powdered Al_2O_3; (4) calorization of cast iron; or (5) lining the crucible with baddeleyite (ZrO_2) or similar material.

Description of hot modulus of rupture and hot crushing strength tests and discussion of results. E. B. HUNT AND R. S. BRADLEY. *Bull. Amer. Ceram. Soc.*, **20** [8] 267–69 (1941).—5 figures.

Effect of firing temperature on properties of grog bodies. A. K. FREBERG. *Ogneupory*, **8** [8–9] 456–62 (1940).—With increasing firing temperature up to 1400°, the resistance of the grog body to pressure under load rises, but gas permeability decreases; porosity and mechanical strength increase to certain limits, after which both decrease. In bodies fired to 1500°, most of the technical properties improve because of a change in the glassy phase which is enriched by more refractory oxides, such as Al_2O_3. M.V.C.

Heating-furnace refractories: I. EVERETT C. HITE AND GILBERT SOLER. *Brick & Clay Record*, **96** [3] 57–58 (1940).—The use of a recently developed flat arch design for billet-heating furnaces provides for improved heat transfer, uniformity of temperature, and fuel economy. Either first-quality or superquality refractories are used, the chief requirement being a high resistance to spalling. Any spalls or drips falling on the billets may result in surface defects in subsequent rolling operations. Side-wall refractories, especially door arches, must also be resistant to spalling. Second-quality brick may be used in the outer side-wall construction. Insulation is used, but care must be taken to prevent overheating of both the refractories and the structural steelwork. The brick used in the piers supporting the water-cooled skids must have high load-bearing properties and good spalling resistance. Superduty and high-alumina brick have given favorable results, although the load-bearing properties have been deficient at times. Semisilica brick appear suitable for this service. Furnace bottoms may be constructed of fireclay, high alumina, and plastic brick or chrome-base plastics, depending on the severity of the service. B.C.R.

History of the refractories industry: I and II. JOHN D. RAMSAY. *Brick & Clay Record*, **96** [3] 54–56; [4] 70–72 (1940).—R. discusses the historical development of this industry. **III.** *Ibid.*, [5] 60, 62.—The advent of such refractories as plastic firebrick, high alumina, superduty, and insulating brick, and high-temperature cements is discussed. Because of the abandonment of many plants, the fire-clay brick capacity is much less than it was in 1929–1930. Silica-brick capacity has changed very little, possibly increasing. B.C.R.

Indexes of the unsuitability of raw dolomite in dependence on its chemical composition. D. A. NIRENSHTEIN. *Ogneupory*, **8** [8–9] 424–30 (1940).—Attempts were made to determine the limits of the ratio of CaO to SiO_2 and the R_2O_3 content which give an indication of the crumbling of dolomite on cooling after firing. Dolomites with a ratio of CaO to SiO_2 less than 2.5 and containing R_2O_3 should not be fired because they will crumble on cooling. M.V.C.

Late developments in open-hearth practice. D. L. MCBRIDE. *Metal Progress*, **39** [6] 717–20 (1941).—Considerable attention is being given to the use of specially prepared hot-top insulation for ingots of killed steel. These prepared insulators are replacing some of the cheaper materials, such as straw, oat hulls, sand, slag wool, and coke breeze. B.C.R.

Manufacture of refractory materials from lime. F. D. STAROSTIN. *Ogneupory*, **8** [8–9] 462–68 (1940).—Experiments showed the possibility of manufacturing lime refractories (with additions of stabilizers containing C_2S and C_3S) on a dicalcium and tricalcium base. M.V.C.

Melted magnesite for the production of highly refractory products. N. I. VORONIN. *Ogneupory*, **8** [8–9] 417–23 (1940).—The stability of chrome-magnesite products with a fused-magnesite base is considerably superior to that of silica or ordinary chrome-magnesite products in the crowns of electric steel-melting furnaces. M.V.C.

Minerals, combustibles, and chemicals used in making insulating materials. JAN OTTO KNIZEK. *Brick & Clay Record*, **97** [5] 52–54 (1940).—K. reviews the different methods of providing a cellular structure in insulating brick. The relative merits and the uses of insulation are discussed. B.C.R.

Petrography of magnesite refractories. A. V. RUDNEVA. *Ogneupory*, **8** [10] 538–43 (1940).—Magnesite fired to 600° remains unchanged; at 800° it shows some signs of dissociation. At 1000° it represents an isotropic mass composed of aggregates, and at 1200° it shows the same characteristics. At 1400° small areas transform into periclase, and the quartz present changes into forsterite. At 1600° the body changes into a fine-grained structure, and at 1800° and 2000° the fine-grained structure changes into periclase while forsterite melts and forms a bond between the periclase grains. Conclusions are as follows: (1) the dissociation of magnesite begins at about 800°; (2) between 800° and 1000° magnesite passes through an unstable form; and (3) beginning at 1400° periclase grains begin to appear in the isotropic and apparently amorphous mass. M.V.C.

Principal physical tests for fire-clay refractories: I. R. S. BRADLEY. *Brick & Clay Record*, **96** [4] 66–69 (1940).—B. discusses in detail the method and equipment necessary for determining the P.C.E. of fire-clay materials. **II.** *Ibid.*, [5] 57–59.—The purpose of the permanent linear change test is to determine the reheat behavior or permanent volume change of fire-clay brick when heated under prescribed conditions. Reheat tests are run at 1600°C. for 5 hr. for superduty brick and at 1500°C. for high heat-duty brick. The procedure for carrying out the test is described, and the types of kilns used are illustrated. B.C.R.

Production of aluminum oxide from Aktash agalmatolite by the Buchner method. K. SHADYBEKOV. *Trudy Uzbekskogo Gosudarst. Univ. Sbornik Rabot Khim.*, **15**, 116–19 (1939); *Chem. Abs.*, **35**, 4553 (1941).—Aktash agalmatolite contains SiO_2 42.98, Al_2O_3 40.69, Sc_2O_3 1.06, CoO 0.75, MgO 0.47, and $Na_2O + K_2O$ 2.03%; loss on ignition is 11.98%. The agalmatolite was ground in a steel and an agate mortar and fired in a muffle furnace at various temperatures and for different lengths of time. The optimum temperature was 550° to 560°, and the time was 2 hr.; a brittle white mass was produced. This was treated in a porcelain dish with H_2SO_4 (density 1.41, 1.51, 1.61, and 1.71). Optimum results were obtained from H_2SO_4 with specific gravities of 1.41 and 1.51. In all cases a slight excess of the acid was used over that required for each of the oxides Al_2O_3, Fe_2O_3, CaO, MgO, etc. The mixture was heated on a water bath at 95° for 5 hr. The pulp was treated with hot water and filtered to separate SiO_2 and other admixtures. In such cases, H_2SO_4 in the solution was neutralized with a base. As a result of this, a definite volume (800 to 1000 cc.) of a colorless solution was obtained. From this, 100 to 200 cc. were taken for the precipitation and determination of Al_2O_3 by treatment with concentrated NH_4OH, followed by heating to 85° until the disappearance of the odor of NH_3. The precipitate was filtered through an ashless filter, washed with hot water, and fired for the preparation of anhydrous Al_2O_3. The silicic acid content in the alumina did not exceed 0.04%. Many of the samples investigated contained no silicic acid. SiO_2 and alumina were determined by the usual gravimetric method. Fe_2O_3 in the solution was determined by titration. $(NH_4)_2SO_4$ was obtained as a by-product, in addition to pure Al_2O_3. Treatment of fired agalmatolite with H_2SO_4 is profitable for the production of Al_2O_3.

Protecting lightweight refractories. A. A. PIROGOV AND A. I. ROÏZEN. *Ogneupory*, **8** [11–12] 560–66 (1940).—Protective linings for lightweight refractory brick lower the gas permeability of the masonry, increase its resistance to thermal shock, and, in some cases, protect it from the effect of slag. For temperatures of 1400° and higher, corundum, aluminous, kyanite, and kaolin-grog linings are recommended. Chromite linings protect brick from the effect of slag. Linings must possess low shrinkage and low thermal expansion; these properties may be obtained by thinning the mixes and selecting a suitable granulometric composition. M.V.C.

Refractories in regenerators of open-hearth furnaces. M. P. NAZAROV. *Ogneupory*, **8** [11–12] 609–13 (1940).—The behavior of silica and grog refractories in the regenerators of open-hearth furnaces is discussed. M.V.C.

Refractories research in the steelworks. J. H. CHESTERS. *Proc. Cleveland Inst. Engrs.* [England], **1939–1940**, No. 3, pp. 103–18.—After stating that research on steelworks refractories involves work of two kinds, viz., fundamental work requiring a long time and work to solve the immediate problems of industry, C. gives examples of both kinds from his own experience. He describes how a three-dimensional diagram of the $FeO–Al_2O_3–SiO_2$ system was constructed with the ternary melting-point diagram as a base. A study of this diagram showed that an increase in alumina content, e.g., from 30 to 40%, would result in increased resistance to attack, because the more aluminous material would require more iron oxide to reduce its melting point to the furnace temperature. It also showed that the ternary eutectic contained only about 10% of alumina; melts containing more or less of this oxide, therefore, would be more or less refractory. C. also describes tests made to ascertain whether used checker brick, even though free from dust and unglazed, are suitable for further service; it was found that they could be used without loss of operating efficiency. In this case the results were applied in practice without any apparent effect on the behavior of the open-hearth furnaces, and a considerable saving resulted. A simple and fairly rapid test by which the thermal shock resistance of refractory brick can be measured is presented. R.A.R.

Refractory products with high mullite and silicon carbide concentrations and their field of application in furnace construction. J. KRATZERT. *Sprechsaal*, **73** [24] 211–13 (1940); abstracted in *Chem. Zentr.*, **1940, II**, 1342.—The properties of mullite and SiC block are discussed, and their use in the construction of furnaces for the iron and steel, metal, ceramic, and chemical industries is described. See "Refractory brick . . .," *Ceram. Abs.*, **18** [11] 302 (1939). M.V.C.

Research problems relating to steelmaking processes. Report of Committee on Physical Chemistry of Steelmaking. JOHN J. EGAN, *Secretary*. *Amer. Inst. Mining Met. Engrs. Tech. Pub.*, No. 1310; *Metals Tech.*, 8 [3] 7 pp. (1941).—Research problems have been outlined to make them available to research laboratories. Their solution would aid in creating a better understanding of the steelmaking process. They are as follows: (I) data involved in the state of equilibrium for the various systems; (II) other physicochemical laboratory problems; (III) problems suited to mill studies, (F) refractories: (1) new refractories for pouring pits, (2) basic material for ladle linings, (3) correct sizing of refractories for the open-hearth furnace, (4) correlation between standard tests and performance of refractories, (5) effect of extremely high forming pressure, (6) nonspalling brick for use in steelmaking, and (7) suitable tests for pouring-pit refractories; (IV) methods of measurement; (V) bibliography. W.D.F.

Selection of refractories in nonferrous metallurgy. R. L. PEVZNER. *Ogneupory*, 8 [11–12] 621–25 (1940).—The service conditions of refractories in converters and reverberatory copper-smelting furnaces are discussed. M.V.C.

Selection of refractories for Vogres steam boilers fired with coal dust. T. P. DERID AND B. A. DEMIDENKO. *Ogneupory*, 8 [8–9] 431–36 (1940).—Refractory linings of Vogres steam boilers must possess high thermal stability, high resistance to slag, and resistance to the effects of flying ashes and gases. Refractories with a high grog content and kaolin products were found most suitable. M.V.C.

Strength of silica brick manufactured from Bobrovskil quartzites in crowns of open-hearth furnaces of the Magnitorsk Metallurgical Combine. V. D. TSIGLER. *Ogneupory*, 8 [5–6] 299–305 (1940).—The causes for the low stability of silica brick made from Bobrovskil quartzites and their composition are discussed. To increase their strength, T. suggests (1) changing the granulometric composition of the mix, (2) introducing admixtures containing iron to obtain more complete tridymitization of the silica; and (3) manufacturing silica brick with a more constant and lower specific gravity. M.V.C.

Testing raw dunite brick in steel furnaces. A. A. POPOV. *Ogneupory*, 8 [10] 520–28 (1940).—Unfired dunite brick were tested in electric open-hearth furnaces and in the linings of steel ladles. Unfired dunite products may replace chrome-magnesite products successfully where they are not subjected to severe changes of temperature. M.V.C.

Uktusskil dunite and its use in the refractory industry. P. S. MAMYKIN, V. V. SAPAROV, AND P. N. D'YACHKOV. *Ogneupory*, 8 [7] 348–58 (1940).—Tests showed the possibility of using Uktusskil dunite in the manufacture of refractories, particularly in the production of fired forsterite refractories. M.V.C.

Using lightweight refractory brick as lining for periodic furnaces for firing porcelain. E. A. LEBEDEV. *Keram. Sbornik*, No. 12, pp. 13–15 (1940).—The use of lightweight refractory brick as a thermoinsulating lining for periodic furnaces was found advantageous because of their durability and the saving in fuel consumption. See "Lining . . ." *Ceram. Abs.*, 19 [3] 68 (1940). M.V.C.

Using silica in Cowpers of blast furnaces. G. I. LUKIANETS AND M. I. LUKIANETS. *Ogneupory*, 8 [8–9] 437–42 (1940).—Observations showed that silica brick are more suitable than grog brick for the cupolas of Cowpers of blast furnaces. M.V.C.

PATENTS

Acid process for extraction of alumina. A. W. HIXSON AND RALPH MILLER (Chemical Foundation, Inc.). U. S. 2,249,761, July 22, 1941 (Aug. 5, 1938).

Brick manufacture. C. L. NORTON (Babcock & Wilcox Co.). U. S. 2,251,687, Aug. 5, 1941 (Feb. 8, 1929).—A method of manufacturing a building block having refractory and heat-insulating characteristics includes the steps of forming and molding an intimate highly aerated liquid mixture of refractory and combustible organic particles, deliquidizing the mixture while substantially preserving its aerated condition, and then firing the block to establish its refractory characteristics and eliminate the organic particles, thereby creating minute voids in addition to those created by aeration.

Porous refractory material. C. S. MATHENY (National Fire Proofing Co. of Canada, Ltd.). Can. 398,156, July 22, 1941 (Nov. 9, 1940).—The method of making lightweight refractory insulating brick comprises mixing the clay with 1 to 50% shredded or comminuted paper, tempering to produce a knurly and fibrous texture, molding to the desired shape, and firing in a kiln to burn out the paper. G.M.H.

Purification of alumina. TAKUO HITOKATAI AND SIGEBUMI MURAKAMI (Syōwa Denkō K. K.). Japan. 133,315, Nov. 17, 1939; *Chem. Abs.*, 35, 4556 (1941).—Crude Al_2O_3 containing oxides of Ti, Fe, and Si is treated with Cl_2 at high temperature in the presence of S and with or without C and washed with dilute alkali, acid, or water to obtain pure Al_2O_3.

Refractory. C. J. KINZIE AND EUGENE WAINER (Titanium Alloy Mfg. Co.). Can. 397,864, July 8, 1941 (Nov. 15, 1939).—A composition suitable for forming refractory masses comprises a refractory material and a zirconate of a metal taken from the group consisting of lithium, sodium, potassium, magnesium, calcium, barium, strontium, and zinc, with or without the addition of acid. G.M.H.

Refractory building material. V. M. GOLDSCHMIDT. U. S. 2,252,317, Aug. 12, 1941 (Feb. 10, 1937).—A refractory comprising about 50 to 80% by weight of material of the group consisting of magnesium orthosilicate and materials rich in such silicate substantially wholly in the form of granules of at least about 0.2 mm. size and about 20 to 50% by weight of refractory material other than the silicate in the form of particles less than about 0.2 mm. size and containing not over about 25% of the orthosilicate and materials productive of it, the refractory being characterized by high resistance to spalling and to load at high temperatures in the fired condition.

Whiteware

Hard porcelain as material for the construction of apparatus. JOS. WALLICH. *Fette & Seifen*, 47, 304–307 (1940); *Chem. Abs.*, 35, 3125 (1941).

Mechanical strength of spark plugs from talc. L. V. OMININ. *Keram. Sbornik*, No. 12, pp. 15–23 (1940).—By lengthening the duration of grinding and increasing the grinding fineness of talc mixes, the mechanical strength of the bodies is increased by about 15 to 20%. The increase in mechanical strength, however, apparently affects the thermal resistance of the body. The increase in the intensity of firing of talc only slightly raises the mechanical strength of the body. Deairing of mixes increases mechanical strength. See *Ceram. Abs.*, 20 [9] 220 (1941). M.V.C.

Particle-size distribution of glazes. J. H. KOENIG AND F. C. HENDERSON. *Jour. Amer. Ceram. Soc.*, 24 [9] 286–97 (1941).—11 references, 13 figures.

Possibility of substituting sodium feldspar for potassium feldspar in porcelain pastes. C. FICAI. *Ceramica*, 3 [4] 149–55 (1941).—The work of investigators on feldspars used in ceramics, the constitution of feldspar minerals, and the function of feldspar in the formation of porcelain is cited as an aid in the study and use of the principal types of Italian feldspars. F. concludes that the characteristics of porcelain pastes which are changed by the substitution of sodium feldspar for potassium feldspar are (1) viscosity at high temperature, (2) transparency of the finished product, (3) thermal expansion, and (4) sound. The two

different feldspars do not seem to affect the elasticity, porosity, shrinkage, color, adaptability to the glaze, and mechanical resistance of the porcelain samples (opinions differ regarding the last property). The refractoriness and viscosity increase with the K_2O content in feldspars. Porcelain containing sodium feldspar is less transparent than that containing potassium feldspar; thermal expansion is higher in sodium feldspar enamels. 49 references. M.V.C.

Pottery produced with the use of dolomite: III, Dolomite earthenware. KŌSUKE HIRANO, SINITIRŌ OGAWA, AND SIGEO SAWAMURA. *Repts. Imp. Ceram. Exptl. Inst.*, **1938**, April, pp. 1–18.—Bentonite (1 to 9%) was added to a dolomite earthen mass, and the changes in physical properties after firing were observed. The bending strength increased gradually from 200 to 250 kgm. per sq. cm. The firing shrinkage decreased somewhat, although bentonite undergoes a marked shrinkage above 800°. Density and true porosity decreased somewhat, while the apparent density showed some increase. The true porosity was increased more by firing to Seger cone 1*a* than by firing to cone 05*a*. This is due to the special expansion of this mass in the range 950° to 1150°. The whiteness, measured by the Pulfrich photometer, was reduced from 80 to 75% by the addition of the bentonite, which, however, was of no practical importance. There was no crazing of glazed specimens when they were treated in the autoclave (12 kgm. per sq. cm.). No linear changes occurred in the heated mixtures. In general, the thermal expansion of the fired mass increased somewhat. Cristobalite formation and the formation of free quartz could not be observed. The impact resistance was improved by the addition of 3% bentonite. **IV, Low-fired porcelain produced with the addition of dolomite.** *Ibid.*, pp. 19–42; abstracted in *Chem. Zentr.*, **1939, II**, 2363; *Chem. Abs.*, **35**, 4928 (1941). —Porcelains were produced from Kosai kaolin, Kawachi feldspar, quartz, and Tsukumi dolomite. The products were white and hard. The addition of bentonite served to impart plasticity to the mass. With a high feldspar content the addition of bentonite resulted in a very low firing temperature (1180° to 1230°). For Parts I and II see "Researches . . .," *Ceram. Abs.*, **16** [2] 68 (1937).

Preparing gas distributors using Alundum disks. S. EDWARD JOLLY. *Ind. Eng. Chem., Anal. Ed.*, **13** [7] 478 (1941).—Details of the construction are given. Illustrated. F.G.H.

Royal China Co.'s automatic stampers decorate 200 dozens per hour. ANON. *Ceram. Ind.*, **36** [4] 90–94 (1941).—An automatic machine for stamping filigree decorations on dinnerware is described. Three obstacles confronting mechanical stamping equipment have been overcome. Uneven ware is carefully gauged and sorted before it enters the machine. The smearing problem has been overcome by using a secret formula in color composition. The problem of feeding has been solved by using manual instead of mechanical feeding. Six stamping machines decorate 100,000 pieces daily. The room temperature method of drying, as originated by the Royal China Co., is described. Jiggered ware is dried under the plant roof while moving slowly on boards suspended on hangers between two synchronized chains. This gives very economical drying because fuel cost is entirely saved. Drying without additional heat increases mold life at least 20%. Illustrated. H.T.

PATENTS

High-tension insulators. WHESSOE FOUNDRY & ENGINEERING CO., LTD., AND A. PUTTICK. Brit. 537,834, July 23, 1941 (Jan. 10, 1940).

Preparing fluorescent materials. G. R. FONDA (General Electric Co.). U. S. 2,252,500, Aug. 12, 1941 (Dec. 7, 1939).—A method of preparing a fluorescent silicate comprises forming a mixture of colloidal gel of silica formed from alkyl organic silicate, a metal compound which will react with the silica to form the fluorescent silicate, and an activator of fluorescent properties, heating to remove volatile constituents from the mixture, comminuting the product, and firing at an elevated temperature to develop fluorescent properties.

Spark plug. P. G. ANDRES (Bowes Seal Fast Corp.). U. S. 2,253,220, Aug. 19, 1941 (July 1, 1940). EMIL KOHOUT AND K. L. INGERSOLL. U. S. 2,252,636, Aug. 12, 1941 (April 27, 1940). G. S. WEINERTH. U. S. 2,251,179, July 29, 1941 (Jan. 9, 1940).

Spark plug. E. E. BIDWELL (Productive Inventions, Inc.). Can. 397,829, July 8, 1941 (July 3, 1939). G.M.H.

Spark plug and method of making. R. J. L. DUTTERER (Defiance Spark Plugs, Inc.). U. S. 2,252,496, Aug. 12, 1941 (March 13, 1940). L. MELLERSH-JACKSON (Aeroflex Laboratories, Inc.). Brit. 537,228, June 25, 1941 (Dec. 6, 1939).

Vacuum-tight metal-to-ceramic seal and method of making. GÜNTHER DOBKE (General Electric Co.). U. S. 2,250,986, July 29, 1941 (Sept. 5, 1940).

Vitreous composition. WERNER DÜSING (General Electric Co.). U. S. 2,252,495, Aug. 12, 1941 (June 28, 1938).—A vitreous composition which, in the form of a plate 1 mm. in thickness, transmits more than 50% of the infrared rays having a wave length less than 4.5 microns and at least 10% of the rays having a wave length as long as 6 microns, the composition comprising 12 to 15 silica, 71 to 76 calcium oxide, and 12 to 15% of one or more oxides selected from the group consisting of barium oxide and zinc oxide.

Equipment and Apparatus

Care of wire ropes—lubrication. WALTER C. RICHARDS. *Mining Congr. Jour.*, **27** [4] 57–60 (1941).—To be kept in good condition a rope must be lubricated frequently. This reduces internal and sheave frictions and protects the exterior from corrosion. The signs of rust and corrosion may not appear on the outside first. A thin oil is used for the inside. It should be thinned either by a volatile solvent or by heat, or the two may be alternated. A heavier oil is used for the outside, the exact type depending on the working conditions. This may be applied (1) by running the rope through a trough of lubricant or through a special device for vertical ropes, (2) at a sheave, or (3) by a brush. W.D.F.

Combination visual and autometric method of optical pyrometry. ERLE I. SHOBERT, II. *Instruments*, **14** [3] 69 (1941).—S. describes the construction and operation of an indicating optical pyrometer suitable for measuring, indicating, recording, and controlling any temperature that can be measured with an optical pyrometer. The accuracy of the instrument decreases as the observed temperature increases, being about 15°C. in the range 850° to 1550°C. and 20° to 30°C. in the range 1550° to 2000°C. A diagram of the instrument is presented. B.C.R.

Dearing fine clay bodies in the plastic form. E. A. HAWK. *Bull. Amer. Ceram. Soc.*, **20** [8] 274–75 (1941).

Determination of water in ceramic masses. A. M. TRAKHTENBERG. *Prom. Stroitel. Materialov.* **2** [9] 36–37 (1940).—The method is based on the use of calcium carbide which reacts with the moisture of the material tested. P.B. & E.S.

Drying troubles: IV. L. R. WHITAKER. *Brick & Clay Record*, **96** [3] 18–20 (1940).—The condensation of water vapor upon the ware in the cold end of the drier may be lessened by increasing the draft at this point. Excessive drying on the top and sides, however, may produce cracks similar to those caused by condensation, and the ware in the center of the car may not be dried sufficiently. Apparently, dry ware that becomes wet soon after its removal from the drier indicates that only the outer surface was dried and that the interior was still wet. To accomplish the best work with the least volume of air and the lowest temperature, short-cutting of the air must be reduced to

a minimum, and the exhaust air must carry as much water as possible without causing too much condensation. **V.** *Ibid.*, [4] 19–21.—W. discusses the operation of a drier on the basis of the length of the drier, construction of the flues, and the air supply, whether under pressure or suction. **VI.** *Ibid.*, [5] 23–24.—In operating waste-heat driers, sufficient kilns must be available to supply the drier with a uniform flow of heat throughout the week or the drier will tend to run wet toward the end of the week. Adequate flues must be provided to allow sufficient atmospheric air to be pulled in by the fan to provide an adequate volume of air for proper drying. Excessive temperatures must be avoided; otherwise steam may form in the interior of the ware, resulting in cracking. **VII.** *Ibid.*, [6] 30–31.—Air entering a drier should be dry except for ware requiring slow drying; in this case a humidity drier may be used economically. Control of drying is accomplished through control of temperature, volume, humidity, air distribution, and car schedule. **VIII.** *Ibid.*, **97** [1] 27–28 (1940).—W. discusses the various factors governing the size of the flue openings beneath the cars. B.C.R.

Electrical resistance furnaces for high temperature. PAUL SCHWARTZKOPF. *Metals & Alloys*, **13** [1] 45–49 (1941).—S. briefly discusses furnaces heated by (1) resistance wire, (2) resistance heating rods on a silicon carbide basis, and (3) heating elements of metals with a high melting point, separated from the furnace atmosphere by a gas-proof protective casing. The latter type is described in detail; it consists of rods or wires of molybdenum or tungsten built into vacuum-tight ceramic tubes. Based on rod (element) temperatures, these elements have a life of 500 hr. at about 1700°C. to 5000 hr. at 1575°C. The life of the element depends largely on the maintenance of a vacuum-tight seal at the ends of the rods. B.C.R.

Electron microscope. A. L. G. REES. *Chem. & Ind.*, **60** [18] 335–37 (1941).—R. gives an account of the development of the microscope. Increase in magnification can result only from improvement of the electron optical lenses through an increase of the numerical aperture and a simultaneous decrease of the spherical aberration. Two useful developments include electron stereomicroscopy and ultramicroscopy. The former is achieved by taking two photographs tilted slightly with respect to one another. When observed under a stereoscope, these give an excellent three-dimensional impression. The ultramicroscopic method, in which the object is illuminated by dark-ground illumination, enables objects far beyond the resolving power of the instrument to be observed. G.R.S.

Hammer mill for clay grinding. ANON. *Brick & Clay Record*, **97** [5] 29 (1940).—Some installations showed improvement in particle sizing and increased output for some clays. Most installations were made to obtain a large amount of fines and to increase the output of the dry pan with which they are run in conjunction. B.C.R.

How to get the most out of your auger. F. S. WINDOPH. *Brick & Clay Record*, **96** [6] 26–28 (1940).—Laminations caused by improper passage of clay through the auger may be due to the following causes: (1) a greater auger pitch than the character of the clay warrants; (2) insufficient or intermittent feed; (3) loose fit of the auger in the lining, permitting the wall of clay to become so thick that it breaks down and allows the clay to move backward over the edge of the thread; (4) a lining worn so thin that the clay slips over it instead of being held tightly against the auger thread. The two most common and costly errors in auger operation are the practice of running machines too fast and that of continuing to run augers and linings after they should be discarded. B.C.R.

Interesting conveyer installation at a clay pit. ANON. *Colliery Guardian*, **162**, 585–87 (1941).—In a recent installation, five sectional belt conveyers are used to carry clay from the working face to the mill. Two conveyers, each 505 ft. long, are end to end and parallel to the working face. Two others carry the clay to the mill. Material unsuitable for use in the mill is diverted by the fifth conveyer and discarded. Fastened to each excavator is a counterbalanced chute lying over the belt; the excavator discharges into the chute which spreads the clay out evenly over the belt. The capacity of the installation is 60 tons per hr.; it uses 8 h.p., and only three men are required to run it. W.D.F.

Measuring the air flow of small fans. ANON. *Bell Lab. Record*, **19** [4] 134 (1940). P.S.D.

Reclaiming ball-mill trunnions. ANON. *Mining Congr. Jour.*, **27** [4] 60 (1941).—The straight part of the worn trunnion is cut away back to the collar at the outer end. The collar is machined to take the replacement sections. The two are bolted together with a long bolt passing through the center of both castings and are arranged to rotate on the axis of this bolt. The joint is preheated and then welded, using a cast-iron rod. W.D.F.

Rotating disk viscometer. P. J. RIGDEN. *Jour. Soc. Chem. Ind.* [London], **60** [1] 18–20 (1941).—A rotating viscometer provides a rapid determination of viscosity of materials within a range of 10 to 10^4 poises. Useful features are rapidity of use and ease of cleaning. Full calibration curves are included. Illustrated. G.R.S.

Silicon carbide varistors. R. O. GRISDALE. *Bell Lab. Record*, **19** [2] 46–51 (1940).—G. discusses the current-voltage characteristics of compressed silicon carbide granules. The electrical characteristics of completed silicon carbide varistors are dependent on the composition and on the heat-treatment to which they are subjected. Methods of producing silicon carbide varistors are described. Variation in performance characteristics with variation in production methods is discussed in connection with current-voltage curves. Advantages and disadvantages of silicon carbide varistors are given. Illustrated. P.S.D.

Theory of drying. A. V. YAROSHEVSKIĬ. *Ogneupory*, **8** [8–9] 451–56 (1940).—Y. presents a critical analysis of the present theory of the process of drying which divides it into several periods sharply distinguished on the curve of the intensity of drying. A formula is given embracing the curve of drying. M.V.C.

Wire-rope constructions and their application. WALTER C. RICHARDS. *Mining Congr. Jour.*, **27** [6] 29–31 (1941).—In a right-lay rope the strands are twisted to the right, as in a screw; if it is also a regular-lay, the wires in the strand are twisted in the opposite direction. In a lang-lay rope the wires in the strand are twisted in the same direction as the strands. There are three types of center: the most used is a hemp-rope center; the wire-rope center or the strand center is used when high temperatures or crushing is encountered. The rope may have round or flattened strands. Preforming frees a rope of internal stresses because the wires and strands are shaped first; this lessens kinking and increases resistance to fatigue. Both fatigue and abrasion tend to destroy a rope. Abrasion is resisted by large wires, fatigue by small. Various arrangements of wires are used to determine the best combination. The simplest arrangement of wires is six around one. To obtain more flexibility, 12 wires are laid around these, and then 18 and maybe even another layer of 24 wires is laid. The 19-wire strand is suitable for most purposes. A rope construction of 6 x 7 means 6 strands of 7 wires each. Various types are arranged with small filler wires between the main ones. The type of rope must be fitted to the machine to be used. Haulage ropes take 6 x 7 and 6 x 19 round strand or 6 x 8 and 6 x 25 flattened strand. Hoisting ropes are 6 x 19 and 6 x 37 round strand or 6 x 25 flattened strand. A lang-lay rope is better able to resist abrasion than a regular-lay, and a flattened strand is still better. W.D.F.

X-ray analysis in industry: I, Industrial applications of X-ray analysis. Applications of the X-ray powder method in industrial laboratory problems. H. P. ROOKSBY. *Jour. Sci. Instruments*, **18** [5] 84–90 (1941).—The experimental technique is discussed. The suitability of certain refractory materials for use in glassmelting tanks is indicated by particular features of the X-ray diffraction patterns. The examination of thermionically active coatings for the cathodes of radio receiving tubes is described. The value of X-ray methods in the study of inorganic luminescence is indicated. Nickel-iron powders, lattice distortion in tungsten, and directional orientation

in rolled metal sheet are considered. 11 figs. See *Ceram. Abs.*, **19** [8] 200 (1940). **Examples of industrial testing of materials by X-ray diffraction.** JAMES A. DARBYSHIRE. *Jour. Sci. Instruments*, **18** [5] 99–100 (1941).—D. describes the application of X-ray diffraction study to (*a*) corrosion, (*b*) insulating materials, (*c*) carbon spray, (*d*) filament wires and heater wires, and (*e*) lead acid accumulators. Six Debye-Scherrer photographs are included. J.L.G.

PATENTS

Gas temperature measuring apparatus. WILFRED H. HOWE (Foxboro Co.). Can. 398,289, July 29, 1941 (Sept. 23, 1940; in U. S. Sept. 23, 1939). G.M.H.

Producing sized ceramic products. E. T. HERMANN. U. S. 2,252,427, Aug. 12, 1941 (Jan. 19, 1939).

Resistor and method of making. R. R. RIDGWAY (Norton Co.). U. S. 2,252,981, Aug. 19, 1941 (May 24, 1939).—An electrical resistor formed as a shaped, self-bonded, coherent, dense, continuous, monolithic, prefused, crystalline structure having alumina crystals as the major phase intergrown with a phase of crystals containing essentially titanium dioxide and a lower oxide and forming an electrically conductive refractory body.

Kilns, Furnaces, Fuels, and Combustion

Anthracite, the principal smokeless fuel. H. J. ROSE. *Ind. Eng. Chem.*, **33** [7] 846–50 (1941).—Anthracite is a smokeless fuel under all combustion conditions. It does not release even a trace of tar when heated. Anthracite is closely sized, hard enough to resist breakage, and noncaking and usually has a high ash-softening temperature. It therefore provides fuel beds of uniform and dependable character. It is the densest and most concentrated of all solid fuels. For these and other reasons, anthracite permits hand firing with maximum cleanliness and convenience and is readily used for automatic firing. More than 99% of the country's anthracite production of 50 million tons annually comes from Pennsylvania, whose reserves are sufficient to last for about 150 years at the present rate of depletion. Illustrated. F.G.H.

Burning natural gas. GEORGE L. BALLARD. *Brick & Clay Record*, **97** [1] 22–24 (1940).—When pressure gas is available, more economical operation of kilns for firing ceramic ware may be obtained by using high-pressure gas in atmospheric burners than by using high-pressure air, as the expense of a blower is eliminated. With high-pressure gas burners in periodic kilns, ware can be fired from 1750°F. to 2950°F. on $2^1/_2$- to 14-day schedules. In some cases, results with proportional mixing type burners were no better than those with high-pressure gas atmospheric burners. Gas consumption for periodic kilns on 7- to 9-day schedules, fired at 2200° to 2400°F., varied from 20,000 to 25,000 cu. ft. of natural gas per M brick. The kilns held about 7500 brick. Recirculation of the products of combustion in periodic kilns firing tile resulted, in one case, in more uniform color and size of the tile. No changes need be made in flue sizes when changing from coal to natural-gas firing. B.C.R.

City gas—the ideal smokeless fuel for domestic and industrial uses. W. L. JONES AND F. E. VANDAVEER. *Ind. Eng. Chem.*, **33** [7] 852–57 (1941).—The magnitude of the smoke problem in urban communities nationally, as well as its causes and economic and health aspects, is reviewed. Energy requirements for residential, commercial, and industrial heating purposes are evaluated, and the proportion of such total requirements supplied by various types of fuels is estimated. The economic possibilities of supplying all energy requirements with clean, refined fuels are discussed. Cleanliness of production, manufacture, distribution, and utilization of gas are emphasized. Specific data are presented on chemical properties of commercial gaseous fuels and their combustion products under typical industrial and residential utilization conditions. Mechanics of gaseous fuel combustion are briefly treated. Comparative economies of residential heating with various types of fuels are indicated. Similar treatment is given to industrial heating processes, the form value of different types of fuel receiving particular emphasis. Special reference is made to the part gas has played in the smoke-abatement problem in the St. Louis metropolitan area. F.G.H.

Clay plant operators' experience when using stokers on kilns. ANON. *Brick & Clay Record*, **99** [1] 19–20 (1941).—The comments of several users of stokers for kiln firing are presented. B.C.R.

Coal savers tested. F. J. MATTHEWS. *Glass*, **18** [5] 142 (1941).—To determine the value of claims that the addition of certain chemicals to coal will improve its burning properties, reduce the amount of smoke produced, reduce clinkering, and eliminate soot deposits, the effect of the addition of the following chemicals to coal was studied: sodium chloride, sodium carbonate, calcium hydroxide, calcium chloride, potassium dichromate, sodium silicate, potassium permanganate, potassium chlorate, boric acid, alumina, silica, ammonium chloride, copper carbonate, copper dichromate, copper chloride, chromium oxide, fluorspar, lead chloride, lead nitrate, manganese dioxide, potassium nitrate, and zinc sulfite. The additions of these compounds, used with and without water in proportions of 4 and 40 lb. per ton of coal, to coals of different coking properties, varying from noncoking to strong coking and containing up to 46% volatile matter, indicated that such treatment did not reduce the amount of soot or tar formation, improve the nature of clinkering (any change tended toward more fluidity in the slag), decrease the amount of smoke (an increase was obtained in some cases), or decrease the amount of sulfur emitted with the gases except in the case of the 40 lb. of lime per ton of coal treatment. Attention to combustion conditions and the proper choice of fuel would give greater satisfaction than the use of chemicals. B.C.R.

Computation of petroleum fractionation. Estimation of A.S.T.M. distillation curves from true-boiling-point distillation analyses. R. L. GEDDES. *Ind. Eng. Chem.*, **33** [6] 795–801 (1941).—The estimation of the A.S.T.M. distillation curves from true-boiling-point distillation curves is a practical problem in the interpretation of theoretical computations of petroleum fractionation. G. presents an improved method of estimating the A.S.T.M. curve from the true-boiling-point curve, which is based on a survey of data from a large number of distillation analyses. It is indicated that the same correlation may be used conversely for the approximate estimation of the true-boiling-point curve corresponding to a given A.S.T.M. distillation curve. F.G.H.

Curran-Knowles process. M. D. CURRAN. *Ind. Eng. Chem.*, **33** [7] 850–52 (1941).—C. describes the Curran-Knowles sole-flue coke oven for producing smokeless domestic and industrial fuel and some installations of this type of oven, in particular, the installation at Millstadt, Ill. The coal is carbonized in a layer approximately 1 ft. thick in a rectangular oven in which the heat is applied to the charge from combustion flues in the oven floor. Illustrated. F.G.H.

Disco, a smokeless fuel. C. E. LESHER. *Ind. Eng. Chem.*, **33** [7] 858–59 (1941).—Low-temperature coke is being made in commercial operation at Pittsburgh from high-volatile coking coal, using the Disco process. The fuel is smokeless, free burning, of firm structure, and easily ignitible. Coals from Illinois, Oklahoma, Utah, Colorado, Kentucky, West Virginia, Ohio, and Pennsylvania have been tested, and it has been found that any coal with suitable coking property can be processed to Disco. Tar is the only by-product. Illustrated. F.G.H.

Firing sewer pipe with stokers and air recirculation system. ANON. *Brick & Clay Record*, **99** [1] 25–27 (1941). B.C.R.

Getting the most out of stoker firing. LARRY A. SHIPMAN. *Brick & Clay Record*, **99** [1] 21–22 (1941).—S. briefly discusses some of the firing problems arising from the use of stoker-fired kilns. B.C.R.

Handling a kiln stoker for best results. WALTER LINDQUIST. *Brick & Clay Record*, **99** [1] 23 (1941).—Although stoker firing provides an economical and efficient method of firing, these advantages will not be achieved unless the stoker is operated properly. Some of the faults frequently committed by operators unaccustomed to stoker firing are as follows: (1) use of too great an excess of air resulting from air pulled in through natural draft, (2) incorrect setting of brick around the bag walls, (3) neglect of the mechanical care of the stoker, and (4) use of incorrect type of fuel. B.C.R.

Hydrogenation of high-volatile bituminous coals. Summary of assays of bituminous coals, subbituminous coals, and lignites. L. L. HIRST, R. L. BOYER, A. EISNER, I. I. PINKEL, AND H. H. STORCH. *Ind. Eng. Chem.*, **33** [8] 1068–72 (1941).—The results are given of liquid-phase hydrogenation assays of four additional bituminous coals made in the Bureau of Mines experimental plant: high-volatile A coals from the Upper Freeport (W. Va.) and the Black Creek (Ala.) beds, high-volatile B coal from the Lower Sunnyside (Utah) bed, and high-volatile C coal from the Indiana No. 4 bed. The results obtained with eight bituminous coals, three subbituminous coals, and two lignites are summarized. F.G.H.

Lowering plant-operating costs. ANON. *Brick & Clay Record*, **93** [6] 13–14 (1938).—Fuel may be saved in firing kilns by insulating the sidewalls of the kilns and by the use of preheated air obtained by redesigning the fireboxes to achieve a recuperative effect. Individual indicating pyrometers are used for each firebox. B.C.R.

Multiple-tunnel kilns. M. S. NELSON AND HEWITT WILSON. *Bull. Amer. Ceram. Soc.*, **20** [8] 270–74 (1941). —3 references, 7 figures.

Production of coke as a domestic fuel. Hayes process for carbonizing coal at low temperatures. G. V. WOODY. *Ind. Eng. Chem.*, **33** [7] 841–46 (1941).—W. describes the Hayes process for carbonizing coal at low temperatures and the production of low-temperature coke in two forms, viz., char and briquettes. Both of these fuels are low in volatile content and are therefore considered smokeless fuels. The indicated cost of production of this fuel is occasioned by the high credits due to high yields of by-products. These high yields are characteristic of this process because of carbonizing at a low temperature and at a rapid rate of heating. The process is simple, and therefore the first, or capital, cost is low. The net result is the production of a smokeless fuel costing only slightly more than the domestic sizes of a good grade of bituminous coal usually marketed in the same district and shipped from the same mines as the fine sizes of coal from which the low-temperature coke is produced. Illustrated. F.G.H.

Smoke ordinances. OSBORN MONNETT. *Ind. Eng. Chem.*, **33** [7] 839–40 (1941).—M. discusses the fundamental requirements in the development of smoke ordinances. F.G.H.

Smoke prevention in St. Louis. RAYMOND R. TUCKER. *Ind. Eng. Chem.*, **33** [7] 836–39 (1941).—Knowledge of the technical methods by which fuel may be smokelessly burned is not enough to achieve successful smoke elimination in cities. Municipal smoke elimination must take into account air pollution from all of the products of combustion, not only from the solid products. Education alone will not accomplish smoke elimination and legislation will not of itself achieve it. It must be made impossible to create smoke. Only low-volatile coal can be permitted for hand-fired furnaces; approved and efficient stokers or other combustion equipment must be used with high-volatile coals. Efforts to pass a law in St. Louis which would make such practices mandatory met with wide opposition from strong minority interests. After the famous "black Tuesday" in the fall of 1939, a committee was appointed by Mayor Dickmann to recommend legislation. No member of this committee was connected with the fuel or fuel-burning industry and was, therefore, not subject to pressure. As a result of its recommendation, legislation was passed under which the Division of Smoke Regulation of St. Louis is now operating. Under this ordinance and by actively following up every complaint, it is making use of public opinion. By cooperative action and education, remarkable progress has been made in eliminating the smoke nuisance from St. Louis. Illustrated. F.G.H.

Stoker-fired periodic kilns. ANON. *Brick & Clay Record*, **93** [4] 32 (1938).—Stoker-fired kilns firing fire-clay brick produce a better and faster firing and eliminate most of the smoke. The kiln is fired from one firebox. The firebox is surrounded on the inside with a semicircular partition within which rests the fire bed of the stoker. The kiln has a capacity of 60,000 brick and is of circular construction. B.C.R.

Stoker firing of kilns. ANON. *Brick & Clay Record*, **99** [1] 16–18 (1941).—The results of a survey covering the firing of various types of brick, tile, sewer pipe, and refractories are reported, showing the amount of fuel saved, improvement in the quality of the ware, and the firing time saved. Both underfeed and overfeed type stokers were used. The cost of equipping the kiln amounts to over $2000. B.C.R.

Top-fired tunnel kiln uses coal to fire clayware economically. PHILLIP DRESSLER. *Brick & Clay Record*, **96** [4] 22–23 (1940).—A top-fired, coal burning tunnel kiln provides an economic method of firing clayware. In this type of firing, crushed coal may be used for direct firing, thus eliminating fireboxes and their inherent problems in operation and maintenance. Coal ash remains granular and does not adhere to the fired ware. The fine coal burns in suspension, and the coarser particles burn on the car platform. Successful operation of the kiln is dependent on the production of a variety of sizes of the powdered coal. The fuel consumption ranges from 5.2 to 7.3% of the fired weight of the ware. B.C.R.

Geology

Acid clay—an agent in chemical weathering. E. R. GRAHAM. *Jour. Geol.*, **49** [4] 392–401 (1941).—Acids commonly recognized as active in geologic processes include water, carbonic acid, and organic acids from plant residues. Colloidal clay acids are now known to be very active in decomposing minerals in the soils of humid and semihumid regions and thus are active in rock-weathering processes. From experiments, the following conclusions were reached: (1) As much as 3.4% of the total calcium in anorthite can be transposed in 107 days to the adsorbed atmosphere of colloidal clay. (2) Clay-adsorbed hydrogen can remove calcium from hornblende and augite. (3) Biotite and microcline are little affected in this time interval. A.C.B.

Adsorption of malachite green by some clay minerals. V. L. BOSAZZA. *Amer. Mineralogist*, **26**, 396–402 (1941).—Aqueous solutions of 0.01 to 0.05% of the dye were used. Both size separates and thin sections were studied. A swelling type montmorillonite took up 0.050 gm. per gm. of sample, while a massive montmorillonite took up only 0.0074 gm. dye per gm. of sample. A kaolinite took up 0.0068 gm. dye per gm., different particles being stained differently. Pyrophyllite stained sky-blue. The dye was remarkably fast. All these stained clays turn red reversibly on the addition of acid. See *Ceram. Abs.*, **20** [4] 101 (1941). W.D.F.

Base-exchange capacity determination as influenced by nature of cation employed and formation of basic

exchange salts. C. A. BOWER AND E. TRUOG. *Soil Sci. Soc. Amer., Proc.*, **5**, 86–89 (1940).—The authors studied the influence of the nature of cations on the results obtained in base-exchange capacity determinations. The exchange capacity of the clay fraction (<2 microns) of a soil of a montmorillonite sample was determined by means of 15 different monovalent and polyvalent cations. The cations involved were H^+, Na^+, K^+, NH_4^+, Ba^{++}, Cu^{++}, Mg^{++}, Be^{++}, Cu^{++}, Mn^{++}, Zn^{++}, Fe^{+++}, La^{+++}, and Th^{++++}. Results obtained with monovalent cations were in good agreement, while those obtained with polyvalent cations gave increasingly higher values with decreases in the strength of the base which the respective cations form. See *Ceram. Abs.*, **19** [10] 242 (1940). R.K.

Brucite. ANON. *Can. Mining Jour.*, **62** [7] 466 (1941).—Pure magnesia will be produced near Wakefield, north of Ottawa, from brucite. The plant will be built under an agreement between the Aluminum Co. of Canada and Canadian Refractories, Ltd. See "Preliminary . . ." *Ceram. Abs.*, **19** [11] 267 (1940). G.M.H.

Ceramic raw materials of the Caucasus. E. I. SERGEEVA AND T. S. LEKAREVA. *Keram. Sbornik*, No. 12, pp. 1–3 (1940).—An analysis is given of the properties, composition, classification, and testing of the ceramic properties of clays and kaolins located in the Caucasus. M.V.C.

Changes in liquefaction and other properties of clays undergoing electrodialysis. V. A. SOKOLOV. *Ogneupory*, **8** [5–6] 282–91 (1940).—A series of clays was subjected to electrodialysis. S. found that electrodialyzed clays liquefy much better than clays not subjected to this treatment. Other properties of clays also change with electrodialysis. M.V.C.

Clay and colloid content determination of soils using a rapid photoelectric procedure. M. L. JACKSON. *Soil Sci. Soc. Amer., Proc.*, **5**, 54–60 (1940).—The coarse and fine clay contents of 38 soils were determined by means of a rapid photoelectric procedure and by the conventional pipette and mechanical-separation procedures for control and comparison. Organic matter was first removed with H_2O_2, and dispersion was effected by a treatment with $NaPO_3$. Turbidity measurements were made with the Evelyn photoelectric colorimeter with a 6600 a.u. wave length light filter. Turbidity was defined as $\log_{10} G_0/G$, where G_0 and G are the galvanometer readings of the suspension medium (water) and the suspension, respectively. For low concentrations of a given suspension, the turbidity was found to be proportional to concentration. Turbidity measurements for coarse clay correlated closely with the percentage of coarse clay found by control methods. The percentages of fine clay from the turbidity and control methods had a correlation coefficient of +0.98. R.K.

Clay minerals and phosphate availability: I, Adsorption of phosphate ions by clay minerals. H. F. MURPHY. *Proc. Oklahoma Acad. Science*, **20**, 79–81 (1940).—Samples of kaolin which had adsorbed P_2O_5 from KH_2PO_4 solution and were subsequently leached with distilled H_2O contained practically no H_2O-soluble P_2O_5 but showed a high content of H_2O-insoluble P_2O_5. In the case of bentonite dust (montmorillonite) a positive test for soluble P_2O_5 was obtained even after leaching with more than 3 liters of distilled H_2O. Montmorillonite fixed very little insoluble P_2O_5. **II, Utilization of adsorbed phosphate by plants.** *Ibid.*, pp. 83–86; *Chem. Abs.*, **35**, 3021 (1941).—Plant tests showed the low availability of the P_2O_5 held by the kaolin-P_2O_5 complex. Greater crop response obtained from the use of the montmorillonite-P_2O_5 complex may have been due to some occluded soluble P_2O_5. Possible explanations are offered for some of the fixation phenomena observed.

Comparison of methods for the determination of soil organic matter. HENRY W. SMITH AND M. D. WELDON. *Soil Sci. Soc. Amer., Proc.*, **5**, 177–82 (1940).—The content of organic matter of 158 samples was determined by four methods of analysis: Schollenberger's titration method, a modification of Robinson's hydrogen peroxide procedure, wet combustion, and a modification of the Walkley-Black method. The Walkley-Black method proved to be twice as fast and one-half as expensive as Schollenberger's method, its nearest competitor in these respects. R.K.

Current and past estimates of phosphate reserves in Tennessee. G. I. WHITLATCH. *Jour. Tenn. Acad. Science*, **16** [3] 310–25 (1941).—Current reserves of phosphate materials have been estimated to be over five billion tons, a total far in excess of any previous estimate for this state. A complete history of former estimates, beginning with the first estimate made in 1906, is given. H.T.

Detection of certain metals in minerals and ores. Ammonium hypophosphite fusion method. H. B. VAN VALKENBURGH AND T. C. CRAWFORD. *Ind. Eng. Chem., Anal. Ed.*, **13** [7] 459–60 (1941).—When fused with ammonium hypophosphite, many minerals and ores are decomposed, the resulting melt often being highly colored. The color of the melt directly or after being treated with water or hydrogen peroxide, is the basis of the tests described for chromium, cobalt, columbium, manganese, molybdenum, tellurium, titanium, uranium, vanadium, and tungsten. F.G.H.

Determination of the efficient surfaces of clay particles with the supermicroscope. W. EITEL AND C. SCHUSTERIUS. *Chem. Erde*, **13**, 322–35 (1940–1941); *Chem. Abs.*, **35**, 3874 (1941).—The determination is made by integration of the positive photograph taken in the supermicroscope. 11 references. See "Ultramicroscopic. . .," *Ceram. Abs.*, **18** [8] 222 (1939).

Determination of exchangeable bases in soils. Rapid micromethods. MICHAEL PEECH. *Ind. Eng. Chem., Anal. Ed.*, **13** [6] 436–41 (1941).—Detailed time-saving procedures for the determination of the exchangeable bases in soils are described, which are suitable for routine soil testing where a high degree of accuracy is usually not required. The bases are extracted with 1 *N* ammonium acetate solution. The exchange capacity is determined by distillation of the ammonia adsorbed by the soil. Calcium is determined volumetrically. Colorimetric methods are employed in the determination of magnesium, potassium, and manganese, utilizing a photoelectric colorimeter. Data tabulated show typical recoveries obtainable with these procedures. Illustrated. F.G.H.

Determination of lead, thorium, and uranium in zircon with regard to measurement of geological time. F. HECHT AND F. KORKISCH. *Mikrochemie*, **28**, 30–63 (1939).—A method is given for the determination of Pb, Th, and U in zircon (and its variety, cyrtolite), only 1 gm. of mineral being required for the determination of these three elements in one weighed portion of material. It is of primary importance for measurements of geological time by the "lead method" that the content of Pb, Th, and U be determined with the greatest possible accuracy. W.N.

Dielectric method for determining soil moisture. JOEL E. FLETCHER. *Soil Sci. Soc. Amer., Proc.*, **4**, 84–88 (1939).—Preliminary work on the dielectric method of estimating moisture contents of soils is presented. The method seems to offer possibilities, particularly for soils *in situ*. Data are presented which indicate the performance of the apparatus in its present state of development. The effect of salts and soil colloids on the method has been investigated. Photographs and diagrams are also presented. R.K.

Feldspar and pegmatite from western Taimir. V. T. POPOVA. *Keram. Sbornik*, No. 12, pp. 45–46 (1940).—Analyses showed that the feldspar of western Taimir is a potassium feldspar of high purity. Pegmatite is of the microcline plagioclase type and is of second-rate purity. M.V.C.

Flotation unit for magnesite. ANON. *Rock Products*, **44** [7] 87 (1941).—The Northwest Magnesite Co., Chewelah, Wash., has built a new flotation unit for processing magnesite to obtain a relatively pure material suitable for refractory, medicinal, and other uses. The rock undergoes a size reduction to 8 in. in a jaw crusher, to 3 in. in a gyratory crusher, and to ¼ in. in a cone crusher. This product is fed to a ball mill operating in a closed circuit with an air separator to produce −65 mesh material which is fed to 32 flotation cells. The resulting purified magnesite is dewatered and fed directly to the rotary kilns for calcination. B.C.R.

Fundamentals in the search for beryllium. PAUL H. M.-P. BRINTON. *Mining Congr. Jour.*, **27** [5] 20–21 (1941).—Beryllium is a valuable alloying element, and its oxide is a refractory of outstanding quality. Beryl is probably the only mineral from which it can be extracted commercially. Beryl usually occurs in pegmatite, and the deposits cannot be worked for beryl alone owing to its low cost; mica or feldspar must therefore be produced at the same time. Recently, prospectors and others have been identifying quartz as phenacite and believe that they have discovered a rich beryllium deposit. Phenacite, however, is still a very rare mineral. In some mining operations, beryl has been overlooked. A better method is needed for detecting small amounts of beryl. W.D.F.

Geological measurement of time by analysis of monazite: I, Determination of lead and thorium. E. KROUPA. *Mikrochemie*, **27**, 165–75 (1939).—K. presents a method for determining lead and thorium in monazite, only 1 gm. of mineral being required for the determination of both these elements in one weighed portion of material. It is of primary importance for measurements of geological time by the so-called "lead method" that the content of Pb, Th, and U be determined with the greatest possible accuracy. As the U content of monazite is always exceedingly small, the figures for Pb and Th are essential for the determination of the approximate age; the figure for U is less important. The method for the determination of U will be given in a subsequent paper. W.N.

Identification of the clay minerals in five Iowa soils by the thermal method. M. B. RUSSELL AND J. L. HADDOCK. *Soil Sci. Soc. Amer., Proc.*, **5**, 90–94 (1940).—The thermal curves for several pure clay minerals, clay-mineral mixtures, and colloids extracted from five Iowa soils were determined. The minerals present in the extracted colloids have been identified by comparing thermal curves of the colloids with similar curves for pure clay minerals and clay-mineral mixtures. All the colloids studied contained a high percentage of montmorillonite and a much smaller quantity of kaolinite. The illite content of the soil colloids could not be estimated from the thermal curves but was calculated from the potassium content. The prominence of the 225°C. endothermic montmorillonite reaction gave some indication of the degree of base saturation of the five soils studied. The average estimated percentages of montmorillonite, illite, and kaolinite for the five soils, based on the thermal curves, chemical composition, and base-exchange capacity data, were 60, 30, and 10%, respectively. R.K.

Industrial uses of precious and semiprecious stones. SYDNEY H. BALL. *Mining & Met.*, **22** [414] 311 (1941).—B. describes the properties and uses of the following stones: diamond, quartz, fluorspar, tourmaline, selenite, agate, garnet, sapphire, ruby, and abrasive minerals. B.C.R.

Kaolins of western Ukraine. S. I. PASTERNAK. *Ogneupory*, **8** [11–12] 585–87 (1940).—The general characteristics of deposits and the properties of kaolin found in this region are discussed. M.V.C.

Linear thermal expansion of adularia. JOSEPH L. ROSENHOLTZ AND DUDLEY T. SMITH. *Amer. Mineralogist*, **26**, 391–94 (1941).—The linear thermal expansion of adularia from Grisons, Switzerland, containing 93% potassium feldspar, was studied from 0° to 1000°C., parallel to the three crystallographic axes. Other thermal changes were also noticed. The mean coefficients of thermal expansion for adularia, all $\times 10^{-6}$, are, for the *a* axis, 0° to 100°C. 16.40 and 0° to 1000°C. 17.62; for the *b* axis, 0° to 100°C. +0.49 and 0° to 1000°C. −0.65; for the *c* axis, 0° to 100°C. 0.49 and 0° to 1000°C. 0.86. Twelve abrupt changes occurred in the rate of expansion, beginning at 120°C. and ending at 950°C. This may be due to the diffusion of sodium feldspar in potassium feldspar. W.D.F.

Measurement of the pH of earths and clays. M. DÉRIBÉRÉ. *Ind. Chim.*, **26**, 589 (1939); *Chem. Abs.*, **35**, 3142 (1941).—The pH value of clay suspensions in H_2O is difficult to obtain colorimetrically because of the adsorption of the dye by the clay, but it can be determined by electrical methods, with a H electrode, by agitating the suspension for a long time, passing H through the suspension for 5 min. before measurement, and using a 5% concentration of the clay in the mixture. In aqueous suspension, clays are partly sol and partly gel, but in salt solutions such as KCl solution, the clay is entirely in the gel state.

Mineral separations reduce quarry costs. F. B. FRANKS. *Rock Products*, **44** [2] 36 (1941).—Froth flotation and centrifuging permit the use of run of mine stone in the manufacture of cement, making selective quarrying to obtain raw materials unnecessary. A plant layout is described in detail. B.C.R.

Modification of the pipette method of mechanical analysis. T. M. SHAW AND E. F. MILES. *Soil Sci. Soc. Amer., Proc.*, **4**, 368–69 (1939).—The following changes have been made in the mechanical analysis procedure: (1) The moisture content of the sample is determined directly on the sample for mechanical analysis rather than on a second sample. (2) The organic matter removed by hydrogen peroxide treatment of the soil is obtained from the difference between the weights of the oven-dried sample and the mineral residue. (3) The silt content of the sample is found by subtracting the total weight of the clay and sand from the weight of the organic matter-free sample. R.K.

Observation of clay minerals using the electron microscope. HIDEO INUZUKA. *Amer. Mineralogist*, **26**, 448–49 (1941).—I. has constructed an electron microscope which has a maximum magnification of 10,000×. A picture was taken of Kibusi clay, a plastic ceramic clay with some organic matter. In the picture, definite crystal forms are not observed, but a semitransparent membrane supporting aggregates of grains may be seen. This membrane may be composed of the organic matter of the clay. W.D.F.

Pendulum method for measuring settling velocities. J. H. MCMILLEN, L. F. STUTZMAN, AND J. E. HEDRICK. *Ind. Eng. Chem., Anal. Ed.*, **13** [7] 475–78 (1941).—Illustrated. F.G.H.

Physical characteristics of the basic components of clay. M. N. KOSHURNIKOV. *Ogneupory*, **8** [5–6] 291–95; [7] 390–94 (1940).—Kaolinite, halloysite, montmorillonite, etc., enter into the composition of most of the clays. Besides quartz, mica, carbonates, Fe_2O_3, and manganese, which are considered as clay admixtures, aluminum hydrate such as hydrargillite, $Al(OH)_3$, and diaspore, $(AlO)OH$, are sometimes observed. Silica in the form of gel may also be present, but always in small amounts. The term "allophane," which means amorphous mixtures of alumina and silica gel, is not suitable. Clays are always composed of crystallized minerals even if they possess colloidal properties to a small degree. On the basis of chemical and mechanical analyses, all the combined alumina and silica are usually related to kaolinite in the studies of clays and in the determination of clay substance; this is not exactly correct. It is possible to use methods permitting a more exact determination of various types of aluminosilicates entering into clays. Knowing the physical properties of these aluminosilicates, it is much easier to determine the characteristics of the clay studied from its components whose properties are known. M.V.C.

Plastic and drying properties of certain clays as influenced by electrolyte content. E. C. HENRY AND A. C. SIEFERT. *Jour. Amer. Ceram. Soc.*, **24** [9] 281–85 (1941).—11 references, 8 figures.

Preparation of base-exchange materials from British clays and minerals. H. INGLESON AND W. H. SULLIVAN. *Jour. Soc. Chem. Ind.* [London], **60** [1] 11–15 (1941).—An examination was made of a number of British clays and minerals to determine the practicability of replacing imported natural base-exchange materials by home-produced substances. A description is given of some of the experimental work which deals principally with fuller's earth and glauconitic sand but also with two china clays. From the results it appears that, although neither of these materials can be made to develop such a high base-exchange capacity as the synthetic zeolites, they compare favorably with imported materials of the same class. The following

base-exchange capacities were found: (1) treated fuller's earth 0.49 lb. CaO per cu. ft., and 0.87 lb. per 100 lb. or 6100 grains $CaCO_3$ per cu. ft. and 10,900 grains per 100 lb.; (2) washed graded glauconitic sand 0.38 lb. CaO per cu. ft. and 0.35 lb. per 100 lb. or 4700 grains $CaCO_3$ per cu. ft. and 4400 grains per 100 lb. G.R.S.

Properties of clay suspensions. G. D. HOBSON. *Journal of the Institute of Petroleum*, **26**, 533–64 (1940).—A capillary viscometer was used to measure the equivalent viscosity of four clays in three different concentrations and at various flows. A plot of viscosity vs. rate of flow showed that, especially at low concentrations, there was little dependence on the flow but the viscosity of some clays at high concentrations dropped rapidly. One curve was sigmoidal. It was found best to stir the clay steadily while making the run. Plotting volume per cent of clay vs. viscosity gave a straight line at lower concentrations, the slope of which rapidly steepens at higher concentrations. Mixtures of clays were more viscous than the sum of the viscosities of each component. The yield values of various suspensions varied from zero to several hundred dynes per sq. cm. The heating of the suspensions of one clay showed that there were two factors, viz., a normal decrease in viscosities and a change due to heating which remains on cooling. One suspension showed a maximum viscosity between 70° and 80°C. Some clay suspensions show no change on aging, while others change considerably over several months. This may be due to volumetric contractions. Particle sizes were obtained from Stokes' law, and the surface distribution was then derived graphically. A connection was sought between this and viscosity, but other factors must be used. A concentric cylinder viscometer was used, but it was not very satisfactory. It could be used for rough measurements of yield values. Suspensions used in it tended to settle out when sheared. Yield values were determined by the slow rotation of a torsion head connected to a cylinder with vanes in the clay suspension. The difference in rotation is plotted against the rotation of the head. At the yield point, this difference suddenly falls off. With one type of mud the line on the graph stayed horizontal. With the more thixotropic muds, the difference increased again and another yield point occurred, etc., giving a saw-tooth curve. This was due to the building up and breaking down of the gel structure. Water bound by the clay was found to be 1 to 25% of the clay. W.D.F.

Properties and uses of the rare-earth metals and their compounds. F. TROMBE. *Chimie & Industrie*, **45** [1] 11–18 (1941).—The use of rare-earth metals or their compounds in glass and enamels is cited. T. presents a comprehensive historical review of the methods of identification and isolation, uses, and properties of the rare-earth metals and their compounds. C.H.L.

Quartzites of the Karaulnoi Mts. G. G. ARISTOV. *Ogneupory*, **8** [5–6] 274–82 (1940).—Quartzites of the Karaulnoi Mts. in the Urals are a high-grade raw material for the production of silica brick. See "Coloring. . .," *Ceram Abs.*, **18** [5] 129 (1939). M.V.C.

Refractory rock from Typus flint clay on the western slope of the Urals. V. N. IVANOV. *Sovet. Geol.*, **9** [9] 35–40 (1939); abstracted in *Chem. Zentr.*, **1940, II**, 1999.—I. describes a deposit of bauxite rock containing 34 to 51.2 Al_2O_3, 20.2 to 47.3 SiO_2, and 1.58 to 20.3% Fe_2O_3. M.V.C.

Semiquantitative estimation of montmorillonite in clays. S. B. HENDRICKS AND L. T. ALEXANDER. *Soil Sci. Soc. Amer., Proc.*, **5**, 95–99 (1940).—Competition experiments between Ca^{++}-H^+, H^+-$C_5H_{10}NH_3^+$, and Ce^{+++}-H^+ are described. Ce^{+++}-H^+ distribution is the most useful of the three for the estimation of montmorillonites. In equivalent concentrations, the micaceous materials preferentially take up H^+, while the montmorillonites take up much more of the Ce^{+++}. A knowledge of the amount of both of these ions held, together with the total exchange capacity, permits an estimation of the amount of montmorillonite present in mixtures. R.K.

Separation of apatite in the flotation of red hematite ores. G. G. BRING. *Jernkontorets Ann.*, **124** [7] 277–312 (1940).—B. describes a laboratory investigation of the separation or precipitation of the apatite present in Swedish red hematite ores, using hydrofluosilicic acid and water glass as separating media. R.A.R.

Sillimanite raw materials of U.S.S.R. K. S. LIAPIN. *Sovet. Geol.*, **9** [9] 26–34 (1939); abstracted in *Chem. Zentr.*, **1940, II**, 1999.—L. presents a review of the deposits of sillimanite, kyanite, andalusite, dumortierite, diaspore, bauxites containing SiO_2 and no iron, and bauxite clays in Russia. M.V.C.

Spodumene pegmatites of North Carolina. FRANK HESS. *Econ. Geol.*, **35** [8] 942–66 (1940).—H. discusses the geology, distribution, and economic features of the spodumene pegmatites of North Carolina. These pegmatites may be grouped as (1) those containing zircon and sphene, (2) those containing uranium and rare earths, (3) those containing lithium and tin, and (4) simpler granite pegmatites containing some beryl. B.C.R.

Studies on humus-clay complexes. HIDEAKI SAEKI. *Mem. Faculty Sci. Agr., Taihoku Imp. Univ.*, **25**, No. 1, *Soil & Fertilizers*, No. 2, 200 pp. (1939); *Chem. Abs.*, **35**, 4137 (1941).—In a study of the formation of Al "silicohumates," the complex was prepared in three ways: (1) by adding a solution of $AlCl_3$ to a solution of Na_2SiO_3 + Na humate; (2) by adding a solution of Na humate to one of Na_2SiO_3 + $AlCl_3$; and (3) by adding a solution of Na_2SiO_3 to a solution of Na humate + $AlCl_3$. The mutual molecular ratio of quantities of Si, Al, and humus was 5:2.5:1, respectively. Flocculation always occurred when the pH was below 7.0. The complex resulting from these mixtures had one isoelectric point near pH 5.2 and another near 3.0. In a similar series of experiments in which $FeCl_3 \cdot 6H_2O$ was used instead of $AlCl_3 \cdot 6H_2O$, the formation of the flocculate showed a tendency similar to that of the Al system. There was, however, no flocculation between pH 2.0 and 2.9 owing to a high dispersity. One isoelectric point was found at pH 4.0. The order of mixing the ingredients had no effect upon the formation of either the Al or Fe "silicohumates." The SiO_2/Al_2O_3 and SiO_2/Fe_2O_3 ratios of the flocculate showed higher values with increasing pH, and at the isoelectric point of the Fe system and the first isoelectric point of the Al system the composition ratios were identical, 1.3. At the second isoelectric point in the Al system the ratio was 0.3. The ratios of Fe_2O_3, Al_2O_3, and SiO_2 (in millimolecules) to humus (g) in the flocculate were inversely proportional to the pH value.

Technically valuable clays of Georgia (kaolins and refractory clays). M. KHANANASHVILI. *Prom. Stroitel. Materialov*, **2** [10–11] 63–66 (1940). P.B. & E.S.

Technological tests of Buzulinskii clays. A. K. KARKLIT AND A. V. MILYUKOVA. *Ogneupory*, **8** [11–12] 576–85 (1940).—Products manufactured from Buzulinskii clays possess high porosity, low temperature of deformation under load, and increased additional shrinkage. Steel ladles manufactured from these clays were fairly satisfactory. M.V.C.

Tektites, puzzle of science. JOHN DAVIS BUDDHUE. *Sci. Amer.*, **164**, 354–56 (1941).—Rough green glass early found in Bohemia was first thought to be artificial, but this was later proved untrue. Other somewhat different varieties of glass were found in Australia, Java, Malay Peninsula, Tasmania, Borneo, Philippines, Indo-China, China, Libya, Sweden, and Texas. All occurrences are near two great circles around the earth. These tektites were not unlike obsidian, but many were far from any volcano. Some think they are meteorites, but they contain 70 to 90% silica, while ordinary meteorites do not contain over 55% silica. Surface markings on these tektites are at least partly due to corrosion. One of the better theories as to their origin is that an ordinary meteorite struck the earth and fused the soil or rock it hit into these tektites. W.D.F.

Theory and practice of flotation: II, Chemistry in flotation. R. W. SCHATZ. *Mines Mag.* [Colo. School Mines], **31**, 117–21 (1941); *Chem. Abs.*, **35**, 3486 (1941).—Organic and physical chemistry fundamentals and the influence of adsorption are discussed. 10 references. For Part I see *Ceram. Abs.*, **20** [6] 156 (1941).

Types of coloring in minerals. T. G. KENNARD AND D. H. HOWELL. *Amer. Doc. Inst. Doc.*, No. 1515; abstracted in *Amer. Mineralogist*, **26**, 405–21 (1941).—The various types of coloring which can occur are described and classified, and criteria for their identification are proposed. The two fundamentally different cases are coloring due to chemical composition and that due to the physical structure. All substances showing chemicocompositional coloring have both a body color and a surface color in various degrees. Malachite and azurite are mainly body color, and gold and silver are mainly surface color. A body color is lightened by continuous subdivision, but a surface color approaches black. Structural colors may be divided into (1) interference colors, as in opal; (2) diffraction colors, as in mother-of-pearl or some agate; (3) Tyndall scattering, as in smoky quartz; (4) large-particle scattering, as with sulfur particles; (5) refraction colors, as are sometimes seen on mineral grains when a Becke line is being observed; and (6) miscellaneous colors. Criteria are given for identifying these. A color shown by a mineral may be the result of two or more causes. W.D.F.

Ultramechanical analysis of soils. A. N. PURI AND B. R. PURI. *Jour. Agr. Sci.*, **31** [2] 171–77 (1941).—A micropipette for the ultramechanical analysis of soils is described. The sources of error in the usual centrifugal methods are discussed, and the new method is shown to be simple, accurate, and capable of being adapted as a routine method in the most moderately equipped laboratories. The treatment of the soil with alkaline permanganate to destroy humus does not affect the inorganic soil colloids. P.S.D.

Use of pipette analysis in clay research. RICHARDS A. ROWLAND. *Trans. Illinois State Acad. Science*, **33** [2] 162 (1940).—In interpreting pipette analyses of clays, R. emphasizes the facts that (1) the data represent only the degree to which it has been disaggregated, (2) it is impossible to completely break up the aggregates of clay, and (3) the particle diameters for each size measured are only equivalent sizes representing a particle, the mass and surface area of which cause it to settle at a rate equivalent to that at which a sphere of the same effective mass might settle. By using different means of disaggregation, large variations in the size analysis of the same clay may be obtained. B.C.R.

X-ray analysis in industry: I, Industrial applications of X-ray analysis. Identification of clay minerals by means of X-ray diffraction diagrams. G. NAGELSCHMIDT. *Jour. Sci. Instruments*, **18** [5] 100–101 (1941).—By allowing clay suspensions to evaporate slowly on a flat surface, specimens are obtained in which the particles are mainly oriented with their basal planes parallel to the plane of sedimentation. Basal spacing reflections obtained from such specimens with an X-ray spectrometer can be identified with more certainty than those obtained from X-ray powder diagrams. This is important, as the basal spacings are the best characteristics for differentiating between various clay minerals or groups of such minerals, particularly if several of them occur in a mixture and their grain sizes are small. J.L.G.

BOOKS AND SEPARATE PUBLICATIONS

Bauxite Deposits of Alabama. WALTER B. JONES. *Geol. Survey Alabama, Bull.*, **47**, 94 pp. (1940); *Chem. Abs.*, **35**, 3931 (1941).—Detailed descriptions are given of many mines and prospects, together with over 100 analyses of ore samples.

Chromite Deposits of Coobina, Peak Hill Goldfield. K. J. FINUCANE. *Aerial Geol. Geophys. Survey N. Australia, W. Australia Rept.*, No. 34, 4 pp.; *Chem. Abs.*, **35**, 5067 (1941).—A large deposit of chromite containing 48% Cr_2O_3 occurs as veins and lenses in serpentine.

Last Million Years; a History of the Pleistocene in North America. A. P. COLEMAN. University of Toronto Press, Toronto, 1941. Price $3.50. Reviewed in *Can. Mining Jour.*, **62** [7] 469 (1941). G.M.H.

PATENTS

Chlorination of titanium-bearing materials. I. E. MUSKAT AND R. H. TAYLOR (Pittsburgh Plate Glass Co.). U. S. 2,253,470, Aug. 19, 1941 (Nov. 30, 1939). U. S. 2,253,471, Aug. 19, 1941 (Feb. 8, 1940).

Machine for use in the froth flotation of minerals. L. S. PETERSEN. Brit. 537,538, July 9, 1941 (Dec. 5, 1938).

Purifying of earthy minerals. WILLIAM FELDENHEIMER. U. S. 2,251,256, July 29, 1941 (Aug. 28, 1936).—In a process for improving the quality of earthy minerals such as a clay slip, the steps comprise bleaching the slip in aqueous suspension with a water-soluble bleaching metal salt of hydrosulfurous acid, the metal being replaceable by an alkaline metal to provide a substantially insoluble metal compound, adding a compound of an alkaline metal capable of forming such an insoluble compound and in quantity sufficient to completely neutralize acidity of the clay slip, and improving the color of and thickening the neutral slip by adding additional compound of the alkaline metal to deposit additional solids at a pH value materially above neutrality and up to a point of excessive alkalinity, at which point additional solids will redissolve and the color will recede.

Chemistry and Physics

Chemical analysis of silica and quartzites. N. O. ZELDIN AND S. T. BALYUK. *Ogneupory*, **8** [7] 395–98 (1940).—The accelerated method is based on the treatment of the silica or quartzite sample with hydrofluoric acid in the presence of nitric acid. M.V.C.

Crystallization in silicate slags and glasses. ERIC PRESTON. *Trans. Faraday Soc.*, **37** [4] 209–20 (1941).—Fused silicates, such as technical glasses and slags, because of their high viscosities, are ideal materials for observations of crystallization processes in supercooled solutions. Eutectic separation is clearly shown to be the simultaneous deposition of different crystalline phases from the liquid phase saturated with respect to each constituent; each material preserves its own crystalline form in contrast to the more generally observed characteristic eutectic structures obtained by the rapid cooling of very much more fluid metallic alloys. P. gives an empirical equation relating the rate of crystal growth to the temperature and viscosity of the supercooled liquid phase which has some theoretical significance and which may be applied to a wide range of silicate glasses. It is probable that such an equation may be of general application in the case of crystallization of supercooled solutions. See *Ceram. Abs.*, **20** [4] 88 (1941). G.R.S.

Detection and quantitative determination of small amounts of uranium in silicate forms including glass. JOSEF HOFFMANN. *Sprechsaal*, **73**, 153–57 (1940); abstracted in *Chem. Zentr.*, **1940, I**, 3963.—The process is divided into 6 parts: (1) Separation of SiO_2: As SiO_2 must be removed completely because it decomposes the NaF during the fusing, the HCl solution of the carbonate extraction treatment is evaporated several times on a water bath (not at 120°); the residue on ignition, evaporated with HF, is treated with a mixture of 10 parts Na_2CO_3 and 3 parts borax, and the solution of the fused mass is combined with the filtrate of the SiO_2 precipitation. (2) Precipitation with H_2S: The sulfide precipitation is made in the presence of Mo in a pressure bottle in the usual way. (3) Precipitation with $(NH_4)_2S$: Cr, Co, Ni, and other ions which disturb fluorescence must be completely removed by repeated precipitation. (4) Precipitation of hydroxide with purest NH_3 free from CO_2, prepared according to directions given: In the second precipitation with NH_3, $FeCl_3$ solution is added to the solution so that it will better adsorb the uranyl ions. (5) The U separation from the hydroxide precipitated with it is made twice from the HCl solution in the presence of $(NH_4)_2CO_3$ with NH_3. To prevent the Ca from going into the U solution, the sec-

ond precipitation is heated for a longer time. In this way the $CONH_2ONH_4$ mixed with the $(NH_4)_2CO_3$ or NH_4HCO_3 is converted into $n(NH_4)_2CO_3$, and the formation of the soluble Ca carbamate is eliminated. The U solution can be boiled down only in the presence of HF in a Pt dish. (6) For the quantitative determination of U, exactly 0.5 to 1 gm. purest NaF is added to the residue on ignition in the Pt dish, covered with hot water, evaporated to dryness, and heated to redness; the residue is transfered to an agate dish. By grinding, a homogeneous mass of U fluoride and Na fluoride is obtained from which beads are made in Pt loops. The bluish fluorescences given off when the mass is irradiated with ultraviolet light are compared with comparison beads of known U content; these permit the determination of the U content between 10^{-6} and 10^{-9} gm. and the valuation up to 10^{-11} gm. U. M.V.C.

Dolomite analysis. N. O. Zeldin and S. T. Balyuk. *Ogneupory*, **8** [5–6] 334–35 (1940).—The suggested chemical analysis of dolomite is based upon the determination of MgO by the oxyquinoline method and of SiO_2 by the gelatin method. M.V.C.

Establishing the field of nonmixable solutions in several silicate systems. Corrections and supplement. D. P. Grigor'ev. *Zapiski Vserossiĭskogo Mineral. Obshchestva*, **68** [1] 27–30 (1939); abstracted in *Chem. Zentr.*, **1940, II**, 1844.—G. states that, in literature on the subject, the limits of the field of unmixable solution for some silicate systems are false or are not shown on the diagrams, e.g., those for the systems SiO_2–Mg_2SiO_4–$CaAl_2Si_2O_8$, SiO_2–MgO–Al_2O_3, and SiO_2–Mg_2SiO_4–$CaMg(SiO_3)_2$. The corrected diagrams are given. See "Differentiation...," *Ceram. Abs.*, **20** [1] 32 (1941). M.V.C.

Microdetermination of calcium and magnesium. A. W. Marsden. *Jour. Soc. Chem. Ind.* [London], **60** [1] 20–23 (1941).—By careful attention to detail, 0.1 to 10 mgm. of calcium may be precipitated as calcium oxalate and titrated with 0.02 *N* $KMnO_4$, centrifuged, dissolved in 0.01 *N* acid, and back-titrated to pH 4.5, using a modified achromatic indicator, with the same order of accuracy. G.R.S.

Photometric method for the determination of magnesium. W. Sherman Gillam. *Ind. Eng. Chem., Anal. Ed.*, **13** [7] 499–501 (1941).—A colorimetric method, based on the use of titan yellow and a photoelectric colorimeter, affords a rapid and reliable means for determining magnesium in quantities ranging from 0.5 to 300 p.p.m. in fertilizers and soil extracts. The colored complex is stabilized by hydroxylamine hydrochloride. The procedure does not involve the separation and purification of any magnesium precipitate and thus eliminates several steps. Calcium, up to a maximum concentration of 800 p.p.m., does not interfere with the determination of 1 p.p.m. of magnesium but should be kept below 500 p.p.m. Similarly, ammonium and phosphate ions should be kept below 600 to 700 and 100 p.p.m., respectively, while aluminum and tin must be absent. The spectral absorption curves for the colored complex and titan yellow were determined by means of a spectrophotometer. In the analysis of several commercial fertilizers, tap water, and soil extracts, good agreement between duplicate determinations was obtained. Results were found to agree well with those obtained by the hydroxyquinolate gravimetric method. Illustrated. F.G.H.

Rapid determination of silica in acid-insoluble silicates. George McClellan. *Jour. Assn. Official Agr. Chemists*, **24** [1] 111–12 (1941).—McC. proposes the following rapid method for determining silica in talc or kaolinitic materials: 0.5 gm. silica is fused with 6 gm. anhydrous Na_2CO_3 at 950° to 1050°C. for 15 min. The melt is dislodged into a 400 ml. beaker and dissolved in HNO_3 (15 ml. + 5 ml. H_2O). NH_4Cl 5 gm., $HClO_4$ 20 ml., and H_2SO_4 10 ml. are added in this order and boiled for 15 min. The mixture is diluted with 150 ml. H_2O, filtered, and ignited. Corrections for impurities are made with hydrofluoric acid. This method gives a 99.6% recovery. R.K.

Reactions at high temperatures: VI, Reaction between calcium oxide and stannic oxide in the solid state. Yasuo Tanaka. *Jour. Chem. Soc. Japan*, **62**, 199–203 (1941); *Chem. Abs.*, **35**, 4654 (1941).—Mixtures consisting of various proportions of CaO and SnO_2 were heated at 1300° for 10 hr., and the resulting products were investigated. It is confirmed that two compounds, $CaO \cdot SnO_2$ and $2CaO \cdot SnO_2$, are formed in the CaO–SnO_2 system. $CaO \cdot SnO_2$ is orthorhombic. The cell constants are $a = 3.93$ a.u., $b = 3.99$ a.u., $c = 3.87$ a.u. For Part III see *Ceram. Abs.*, **20** [4] 105 (1941).

Spinel group. A. N. Winchell. *Amer. Mineralogist*, **26**, 422–28 (1941).—W. gives a square diagram with $FeCr_2O_4$ and $MgAl_2O_4$ on opposite corners and the refractive index and specific gravity plotted on the square. Another diagram is given for $FeAl_2O_4$, $MgAl_2O_4$, and $ZnAl_2O_4$, which are probably miscible in all proportions. Spinel, $MgAl_2O_4$, can pick up as much as 60% Al_2O_3 in crystal solution. The iron in spinel can exist as Fe_2O_3 without destroying the crystal structure. A diagram of two ternary systems joined by their common side, $FeFe_2O_4$–$MnFe_2O_4$, the other two components being $ZnFe_2O_4$ and $MgFe_2O_4$, is presented. Only the specific gravity is given on this diagram as the refractive indices are not known. W.D.F.

System CaO–$5CaO \cdot Al_2O_3$–CaF_2 and the stability of tricalcium aluminate. W. Eitel. *Zement*, **30**, 17–21, 29–32 (1941); *Chem. Abs.*, **35**, 4274 (1941).—Thermal analysis gives a preliminary phase diagram of the system CaO–$5CaO \cdot Al_2O_3$–CaF_2, which is one of the simplest eutectic types, without mix crystals and field of primary precipitation of $3CaO \cdot Al_2O_3$. In the presence of CaF_2 as mineralizer, tricalcium aluminate completely decomposes into free lime and $5CaO \cdot 3Al_2O_3$ at temperatures of 1100° to 1300°. The phase diagram of Rankin for CaO–Al_2O_3 must, therefore, be corrected on the side of the basic lime-aluminate mixtures. The melts are characterized as to their constitution by means of roentgenographic (powder diagrams) and microscopic methods; the forms of the crystal species are described.

Ternary system MgO–Al_2O_3–Cr_2O_3. T. E. Krasenskaya, Ya. N. Yasinovskiĭ, and V. V. Goncharov. *Ogneupory*, **8** [5–6] 329–34 (1940).—No chemical compositions were present in the ternary system MgO–Al_2O_3–Cr_2O_3 in the vicinity of MgO. The lowest temperature of melting measured corresponds to 10% Cr_2O_3, 30% Al_2O_3, and 60% MgO. M.V.C.

Use of bromate in volumetric analysis. Determination of arsenic and antimony using internal indicators at ordinary temperatures. G. Frederick Smith and R. L. May. *Ind. Eng. Chem., Anal. Ed.*, **13** [7] 460–61 (1941).—Györy's method for the determination of arsenic and antimony by titration of strong hydrochloric acid solutions of the trivalent elements, using potassium bromate with methyl orange or indigo sulfonate as internal indicators, requires that the reaction be carried out at 80° to 90°C. The authors describe the use of three internal oxidation indicators of the irreversible type in the Györy procedure, by means of which the oxidation of arsenic and antimony by bromate can be carried out at ordinary temperatures and over a wide range, from low to high hydrochloric-acid concentrations. F.G.H.

Use of silicomolybdic acid indicator before volumetric oxidation of iron. Albert C. Titus and Claude W. Sill. *Ind. Eng. Chem., Anal. Ed.*, **13** [6] 416–18 (1941).—A new method for the volumetric determination of iron uses silicomolybdic acid indicator in showing the beginning of ferrous ion oxidation. *N*-phenylanthranilic acid indicator shows the end of that oxidation with standard potassium dichromate solution. The volume of solution used between the two color changes is equivalent to the iron being determined. F.G.H.

Wetting agents. F. E. Bartell. *Ind. Eng. Chem.*, **33** [6] 737–40 (1941).—Much of the development of wetting agents and their technical applications has been of an empirical nature because no suitable method for a detailed evaluation of these products has been available. To evaluate a given wetting agent, information should be available concerning the following properties: its surface tension lowering properties when in water and in organic

liquids; its interfacial tension lowering properties when in systems of water in contact with given organic liquids (immiscible or only slightly miscible in water); its interfacial tension lowering properties in systems of given liquids against given solids. Information on the latter can be obtained through measurement of adhesion tension values, which necessitates the measurement of contact angles. Illustrated. F.G.H.

X-ray analysis in industry: I, Industrial applications of X-ray analysis. Application of X-ray methods to the determination of phase boundaries in metallurgical equilibrium diagrams. W. HUME-ROTHERY AND G. V. RAYNOR. *Jour. Sci. Instruments*, **18** [5] 74–81 (1941).—The relative advantages of the X-ray and classical methods for the determination of phase boundaries in metallurgical systems are discussed. 9 figures. **Applications of X-ray analysis methods to steelworks' problems.** A. H. JAY. *Ibid.*, pp. 81–84.—J. describes the examination of silica, magnesia, and fire-clay refractories and shows that X-ray data on raw material and fired products may be of considerable value in determining the suitability of certain minerals for use as refractories. The changes in constitution and crystalline texture during service are discussed. Metallurgical problems associated with chromium magnet and silicon transformer steels and oxide inclusions in steels are also discussed. 2 figures. J.L.G.

SEPARATE PUBLICATION

Phenomenon of Rupture in Solids. W. WEIBULL. *Ing. Vetenskaps Akad., Handl.*, No. 153, 55 pp. (1939); *Bldg. Science Abs.*, **13**, 118 (1940); *Chem. Abs.*, **35**, 3870 (1941).—Extended investigations showed that the rupture in solids can follow two fundamentally divergent courses resulting in different mathematical expressions for the probability of rupture. To facilitate the numerical computation of the distribution constants by arithmetical methods, formulas are deduced and values are tabulated. The theoretical investigations also deal with series comprising two or more components. As experimental evidence for the theory, two test series are shown which illustrate the two foregoing possibilities. See "Statistical . . . ." *Ceram. Abs.*, **19** [3] 78 (1940).

PATENTS

Chromic oxide pigments. J. W. AYERS (C. K. Williams & Co.). U. S. 2,250,789, July 29, 1941 (Nov. 18, 1940).

Manufacture of alkali metal silicate solutions. D. B. CURLL, JR. (Philadelphia Quartz Co.). U. S. 2,251,515, Aug. 5, 1941 (Jan. 23, 1939).

Manufacture of white lead. A. W. FERGUSON (Oxides, Inc.). U. S. 2,250,756, July 29, 1941 (Sept. 26, 1938).

Production of tin oxide. ÁKOS PINTÉR. U. S. 2,250,552, July 29, 1941 (June 8, 1939).

Zinc chromate. R. W. LEISY (New Jersey Zinc Co.). U. S. 2,251,846, Aug. 5, 1941 (April 29, 1940).—A pigment consists essentially of a basic zinc chromate having the formula $5ZnO \cdot CrO_3 \cdot 4H_2O$, the pigment being substantially free of water-soluble salts.

General

Add to workers' pay and company profit with wage-incentive systems. T. R. LODER. *Ceram. Ind.*, **36** [3] 72–74 (1941).—Modern profit-sharing and bonus systems increase labor's output, thereby raising wages and cutting unit manufacturing costs. Information obtained from experience in the enamel shop of the Cavalier Corp. is presented. H.T.

Development of the ceramic industry in India. N. V RAGHUNATH. *Electrotechnics*, **12**, 24–27 (1939); *Chem. Abs.*, **35**, 3047 (1941).—The industry in India is compared with that in Germany, England, Switzerland, and the U. S., and the scope of further development is indicated.

Dust. ANON. *Brick & Clay Record*, **96** [4] 24–28 (1940).—A discussion of the problem of dust in ceramic plants is presented which covers the medical aspects, quantitative determination, and various means of eliminating the dust hazard in plants. B.C.R.

Dust-collecting system. ANON. *Brick & Clay Record*, **93** [4] 30, 32 (1938).—The installation of a dust-collecting system in a silica-brick plant has materially reduced maintenance costs due to the less frequent need of lubrication, increased life of bearings, and reduced amount of belt dressing required. B.C.R.

Economical dust control with low-resistance exhaust systems: IV, Filter connection and fan selection. F. F. KRAVATH. *Heating & Ventilating*, **38**, 33–35 (Feb., 1941).—K. discusses the importance of proper connections for the filter and exhaust fan. With proper connections, the resistance loss across the filter is a large fraction of over-all resistance loss, but the over-all loss may easily become several times the filter loss when the assembly is poorly designed. The size of the filter must be selected not only for performance but also for low resistance characteristics. It is false economy to scrimp on the size of the filter, as savings in first cost will be replaced by increased maintenance costs and power consumption. Size is an important consideration in fan selection also. For a series of similar fans, capacity is directly proportional to the square of the diameter of the fan wheel, and a small fan must therefore be operated faster than a large one. Frictional loss in the bearings, leakage, frictional resistance of the air moving over the fan parts, and shock losses are also discussed. To secure the most efficient fan, it is essential to carefully select the proper size, the most efficient type, and the best workmanship. **V, Summary—a sample system.** *Ibid.*, p. 33 (March, 1941).—A model exhaust system, embodying the requirements outlined in earlier papers, is briefly described and illustrated. The yearly saving over the cost of an "old" system having all the faults considered in the discussions, under normal operation, is estimated to be $1800. **VI, Plenum chamber systems.** *Ibid.*, pp. 36–38 (April, 1941).—In the pneumatic design of branched systems, it is important to maintain low resistance between the branches and the outlet to obtain equal velocities in the branches. This condition is attained at its best by the use of a plenum chamber which consists of a large box or tank, under pressure or suction, from which the various branch pipes emanate. As there is no appreciable velocity within the chamber, it also acts as a settling chamber; much material may be precipitated there, and the exit velocity to the final filter or fan may be appreciably reduced, as the high conveying velocity is not needed at the outlet. Several types of plenum chambers are described and illustrated. In one type, the plenum is located below the machines it serves, so low that the material caught can slide by gravity into the plenum; no more than the most meager branch velocity is necessitated, and savings in power and maintenance are effected. In another type, the grinders or other machines are built into the plenum chamber, or at least attached to it, so that no contraction in cross-sectional area of the hood occurs, and the material slides by gravity into the plenum, thus avoiding any conveying velocity. This system requires a conveyer for the removal of the precipitated material and a storage tank. When it is not necessary to avoid outside air contamination, a plenum with a sufficiently large cross section is equipped with a tall tapering evase stack instead of a filter, with a resultant over-all loss of less than 1 in. water gauge. K. stresses the great benefit to be derived from a study of the science of dust control by the company's own engineers. For Parts **I–III** see *Ceram. Abs.*, **20** [4] 106 (1941). F.S.M.

Experimental study of inhibitory effects of aluminum compounds in silicosis. LEROY U. GARDNER, MORRIS DWORSKI, AND ANTHONY B. DELAHANT. *Bull. Amer. Ceram. Soc.*, **20** [8] 281, 284 (1941).

Industrial health service for the small plant in the ceramic industry. HUNTINGTON WILLIAMS, WILMER H. SCHULZE, AND JOHN M. MCDONALD. *Bull. Amer. Ceram. Soc.*, **20** [8] 285–87 (1941).

Pittsburgh Plate Glass Co. ANON. *Pittsburgh People*, **1** [1] 7–9 (July, 1940); reprinted in *Bull. Amer. Ceram. Soc.*, **20** [8] 288–90 (1941).

Prophylactic use of sulfonated oil in cement dermatitis. I. PINCUS. *N. Y. State Jour. Med.*, **40**, 1391–93 (1940).—P. presents two cases of cement dermatitis which resisted all attempts at permanent cure until sulfonated castor oil was used instead of soap. The irritant action of soap is based on the type of fatty acids and the alkaline reaction. The mixed fatty acids in sulfonated castor oil show a minimum irritation, and the pH is slightly on the acid side. F.S.M.

Public notice of the German Minister of Labor concerning decisions of the German Committee for Dust Protective Apparatus, Jan. 30, 1940. *Reichsgesundheitsbl.*, **15**, 283–87 (1940).—The published regulations relate principally to protection for sandblasters. Each must have a positive pressure helmet which must have sufficient excess pressure and an air supply of at least 80 liters per min. The helmet must be constructed so as to prevent the air from decreasing below that amount; the air supply must be free from dust and oil, and there must be an adjustable contrivance for heating which will provide a temperature of at least 20°C. It is recommended that air be brought in by special ventilators, and direct connection with the ordinary compressed air supply is allowed only temporarily and only if the other conditions are fulfilled. Three commercial German helmets meet the specifications (one Auer and two Draeger); others have been rejected. F.S.M.

Resuscitation after electric shock. C. F. DALZIEL. *Elec. West*, **86**, 38–42 (April, 1941).—Several first-aid techniques for the electrical worker are presented. The prone pressure (Shaefer) method and pole top method are described, with the aid of numerous illustrations. The various organic causes of death from electric shock, the treatment of shock, and safety measures are fully discussed. F.S.M.

William Schlake. ANON. *Brick & Clay Record*, **96** [5] 26 (1940).—William Schlake was called the "Grand Old Man" of the brick industry. A short account of his life is presented. B.C.R.

Shop kinks and short cuts. ANON. *Ceram. Ind.*, **36** [4] 74–82, 98 (1941).—Novel ideas applicable to various operations in ceramic plants are listed; these were taken from practice and contributed by pottery, glass, and porcelain enamel plants. Illustrated. H.T.

Silicosis phenomena produced by polishing with artificial abrasives. J. HAGEN. *Arbeitsschutz*, **1940**, No. 2, pp. 43–45; *Chimie & Industrie*, **44**, 117 (1940); *Chem. Abs.*, **35**, 4929 (1941).—While the artificial abrasive itself is practically harmless, the binder (20% of the total weight), which is generally composed of kaolin and feldspar, can contain up to 25% SiO_2 and can produce symptoms of silicosis, generally first degree, with chronic bronchitis. The observed silicosis never reaches the seriousness observed when sand is used as abrasive.

Silicosis from porphyry. Subacute silicosis. E. GAUBATZ. *Fortschr. Gebiete Röntgenstrahlen*, **62**, 395–404 (1940).—G. discusses the dangerous effects of granites, porphyries, basalts, etc., and presents case histories and pictures of silicosis in workers engaged for 9 months, 10 years ago, in dry drilling in a tunnel through porphyry containing quartz and orthoclase in equal parts. Of the 6 drillers employed, 3 died of silicosis and 2 are suffering from medium to serious silicosis. Two workers employed in carrying away the material are still free of symptoms. Drilling and crushing under the conditions described result in silicosis over a period of 1 to 3 years. F.S.M.

Sources of error in investigation of efficiency of dust-collecting equipment. K. GUTHMANN. *Stahl & Eisen*, **60**, 253–54 (1940).—Operating efficiency depends principally on particle size and not on velocity of fall. F.S.M.

BIBLIOGRAPHY ON RELATIONSHIP BETWEEN COEFFICIENT OF THERMAL EXPANSION AND COMPOSITION OF GLASS*

COMPILED BY KUAN-HAN SUN AND ALEXANDER SILVERMAN

Introduction

Since Winkelmann and Schott's comprehensive studies on the calculation of various properties of glass from its composition, the subject has received much attention in the last forty-five years. The existing data and knowledge of the constitution of glass are not yet sufficient to permit the assumption of a general relationship to fit all glass systems and all limits of composition. Only approximate generalized formulas and factors for wide ranges and accurate expressions for limited ranges of composition are possible.

The writers have already reviewed the relationship between density, refractive index, and refractivities of glass and its composition.[1] The present bibliography cites literature on the relationship between coefficient of thermal expansion and composition. A general survey shows that the rule of linear addition holds approximately for coefficients of expansion except for boric oxide and, to some extent, alumina-containing glasses.

Three abstract journals, *Ceramic Abstracts* of the American Ceramic Society, abstracts in the *Journal of the Society of the Glass Technology*, and the *Chemical Abstracts* of the American Chemical Society, were used in compiling the bibliography. It covers a period of about forty-five years, from 1894 when Schott's important paper was published to 1939. A few papers published in 1940 or in 1941 are also included. Except for papers published in *Jour. Amer. Ceram. Soc.* and *Jour. Soc. Glass Tech.*,† all papers have been given an abstract reference for quick consultation. It is hoped that the list covers all important references in the field. Abstract journals, however, sometimes miss an article or fail to classify it properly. Authors, moreover, may discuss the subject under a title which fails to reveal the full content. Some references in this list were located through cross references in other papers. The writers intend to read all of the papers in the list, and supplementary material may possibly be found. Most books on glass technology discuss the relationship between composition and thermal expansion. Only a few important English, German, and French books are included in this list.

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